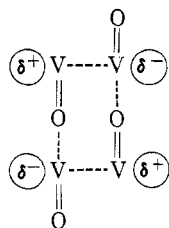


complex indicates that one of the vanadyl oxygen atoms in each molecule is interacting with a vanadium atom in another molecule. A plausible arrangement is



As a consequence of this interaction, the effective charge of one vanadium atom in each pair increases while that of its partner decreases. The result should be an increase in the interaction between the paired vanadium atoms.

We can offer no explanation for the fact that J (H,Cl) is somewhat lower than the other exchange integrals, except to suggest that it may result from a crystal packing effect which somehow causes an increase in the V-V distance.

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Amides as Ligands. VI. Spectrochemical Studies of γ -Thiobutyrolactam and N-Methyl- γ -thiobutyrolactam Cobalt(II) Complexes¹

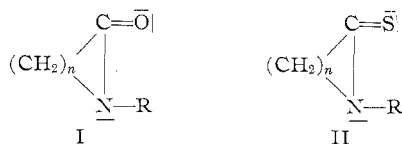
By STANLEY K. MADAN AND MICHAEL SULICH²

Received March 21, 1966

The syntheses, electronic absorption spectra, infrared spectra, magnetic susceptibilities, and conductance measurements of a series of cobalt(II) complexes of the general formulas $[\text{Co}(\text{TbuL})_4](\text{ClO}_4)_2$, $[\text{Co}(\text{NMTbuL})_4](\text{ClO}_4)_2$, $[\text{Co}(\text{TbuL})_2\text{X}_2]$, and $[\text{Co}(\text{NMTbuL})_2\text{X}_2]$ (TbuL = γ -thiobutyrolactam, NMTbuL = N-methyl- γ -thiobutyrolactam, and X = Cl, Br, I, SCN, and NO_3) are described. The usual ligand field parameters Dq , B' , and β are calculated for these complexes. The parameters indicate that these complexes are tetrahedral and sulfur coordinated. The ligands TbuL and NMTbuL are each assigned a position relative to the other sulfur-containing donors in the spectrochemical series. With NMTbuL, an inductive effect, rather than a steric effect, previously observed for some fully substituted amides³ and cyclic lactams,⁴ is found to exist for the coordinated thiolactam. The $[\text{Co}(\text{NMTbuL})_2(\text{NO}_3)_2]$ complex seems to possess an octahedral stereochemistry, a conclusion based on the electronic spectra, infrared spectra, and magnetic moment.

Introduction

The spectral and donor characteristics of a series of lactams with the general formula I (when $n = 3, 4, 5$ with R = H and CH_3) have been recently studied.^{4,5}



The spectral parameters Dq and β have been measured for these lactams with nickel(II) perchlorate and chromium(III) perchlorate, in an octahedral field. However, the thiolactams^{6,7} of the general formula II (when $n = 3$ with R = H and CH_3 or when $n = 5$ with R = H) produce tetrahedral coordination for the cobalt(II) ion.

Pursuant to our interest in substituted amides as ligands and sulfur as a donor atom, we have synthesized a series of cobalt(II) complexes with γ -thiobutyrolactam (TbuL) and N-methyl- γ -thiobutyrolactam (NMTbuL). We have measured the electronic parameters characterizing TbuL and NMTbuL as ligands and have assigned each a position relative to the other sulfur-containing donors in the spectrochemical series, in a tetrahedral field.^{6,8-10} In addition, we have examined the effect on the Dq parameter of substituted and unsubstituted five-membered thiolactam coordinated to cobalt(II) perchlorate in a tetrahedral field.

Experimental Section

All materials used were reagent grade. The N-methyl- γ -butyrolactam was purchased from Aldrich Chemicals and was purified by vacuum distillation. The middle fraction collected at 80° (10 mm) (torr) was used for the preparation of NMTbuL. The γ -butyrolactam was used in the synthesis of TbuL without further purification. Fisher spectral grade nitromethane was employed for the spectral and conductance measurements. Anhydrous cobalt(II) iodide and cobalt(II) thiocyanate trihydrate were obtained from Alfa Inorganics.

Analytical Work.—Carbon, hydrogen, nitrogen, and sulfur analyses were performed by Weiler and Strauss, Microanalytical

(1) Presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 14, 1966.

(2) Based in part on a dissertation to be submitted by M. Sulich to the Graduate School of the State University of New York at Binghamton in partial fulfillment of the requirements for the degree of Master of Arts, 1966.

(3) R. S. Drago, D. W. Meek, M. D. Joeston, and L. LaRoche, *Inorg. Chem.*, **2**, 124 (1963).

(4) J. H. Bright, R. S. Drago, D. M. Hart, and S. K. Madan, *ibid.*, **4**, 18 (1965).

(5) S. K. Madan and H. H. Denk, *J. Inorg. Nucl. Chem.*, **27**, 1049 (1965).

(6) S. K. Madan and C. Goldstein, *ibid.*, **28**, 1251 (1966).

(7) This work.

(8) R. L. Carlin and S. L. Holt, *Inorg. Chem.*, **2**, 849 (1963).

(9) F. A. Cotton, O. D. Faut, and J. T. Mague, *ibid.*, **3**, 17 (1964).

(10) S. K. Madan and D. Mueller, *J. Inorg. Nucl. Chem.*, **28**, 177 (1966).

Laboratory, Oxford, England. Metal analysis was done by a complexometric titration with EDTA.¹¹ Perchlorate and nitrate content was determined by a gravimetric procedure.¹²

Preparation of Compounds.—The ligands TBuL and NMTBuL were synthesized from γ -butyrolactam and N-methyl- γ -butyrolactam, respectively, by the reaction of phosphorus pentasulfide in xylene by a general procedure outlined by Mecke and Mecke.¹³ The crude product obtained on filtering after boiling γ -butyrolactam with phosphorus pentasulfide in xylene was pale yellow. By repeated recrystallization from xylene a white crystalline product was obtained. This crystalline solid had a sharp melting point of 112–113°. The product obtained after boiling N-methyl- γ -butyrolactam with phosphorus pentasulfide in xylene was reduced in volume by using a Rinco evaporator. The pale yellow liquid remaining was vacuum distilled. The fraction collected at 110–112° (5 mm) (torr) was pure NMTBuL. Unless otherwise indicated, all complexes of TBuL and NMTBuL were prepared as follows.

Tetrakis(γ -thiobutyrolactam)cobalt(II) Perchlorate.—Hydrated cobalt(II) perchlorate, $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.10 g, 0.003 mole), was dehydrated by stirring (magnetic stirrer) for approximately 2 hr at room temperature with 100% excess of 2,2-dimethoxypropane (DMP).¹⁴ To the above reaction mixture was added TBuL (1.21 g, 0.012 mole) dissolved in a minimum quantity of hot DMP. When the reaction mixture was stirred vigorously, a crystalline substance separated. The substance was filtered and washed with small amounts of DMP and anhydrous ether. The compound was air dried and stored in a desiccator. It is soluble in most of the common organic solvents with decomposition. In the solid state it is stable up to 2 days at room temperature. When stored in a refrigerator it is stable up to 3 or 4 weeks.

Dichlorobis(γ -thiobutyrolactam)cobalt(II).—This compound was synthesized by the method outlined for the perchlorate complex, with a metal to ligand ratio of 1:2. The complex is fairly stable to air. It is soluble in almost all of the common organic solvents. No visible decomposition was observed in nitromethane or acetone. However, on prolonged standing of these solutions, there appears to be a slight change in the color.

Dibromobis(γ -thiobutyrolactam)cobalt(II).—It was prepared by the same general procedure described for the chloride. The solubility behavior is very similar to that of the chloro complex.

Diiodobis(γ -thiobutyrolactam)cobalt(II).—The complex was synthesized by dissolving anhydrous cobalt(II) iodide (1.25 g, 0.004 mole) in 6 ml of hot 1-butanol to which was added ligand (0.81 g, 0.008 mole) dissolved in 10 ml of 1-butanol, filtered and washed with anhydrous ether, and then stored in a desiccator. This complex decomposes within a few days at room temperature. Its stability improves when it is stored in a refrigerator. Solubility behavior is similar to the corresponding chloro and bromo complexes, but the nitromethane and acetone solutions are much less stable than the chloro and bromo compounds.

Dinitratobis(γ -thiobutyrolactam)cobalt(II).—Hydrated cobalt(II) nitrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.75 g, 0.006 mole), was digested with 100% excess DMP for 2 hr at 30–40°. The resulting solution was evaporated almost to dryness. The residue was dissolved in a small amount of 1-butanol to which was added the ligand (1.21 g, 0.012 mole) dissolved in a minimum quantity of 1-butanol with vigorous stirring. The resultant solution upon cooling in a refrigerator yielded no product. Petroleum ether (bp 35–54°) was added and the resulting oily material was slightly warmed and, followed by vigorous scratching, produced a crystalline product. The coarse crystals were filtered and washed with a small amount of 1-butanol and dried for a few days in a desiccator. These crystals dissolve in almost all organic solvents with extensive decomposition.

$\text{Co}(\text{TBuL})_2(\text{SCN})_2$.—Neither the above method nor several others produced a pure sample of this compound. The oils or oily solids obtained were not characterized.

Tetrakis(N-methyl- γ -thiobutyrolactam)cobalt(II) perchlorate.—Cobalt(II) perchlorate hexahydrate (1.098 g, 0.003 mole) was dehydrated with a 100% excess of a 2,2-dimethoxypropane (DMP) by stirring for 2 hr at room temperature. The resulting rust-colored solution then was treated with NMTBuL (1.38 g, 0.012 mole). When these solutions were mixed, a product was immediately obtained. The crystalline product was collected, washed with several portions of DMP and dry ether, and dried in a desiccator. It is stable to air oxidation and is soluble in most of the common organic solvents.

Dichlorobis(N-methyl- γ -thiobutyrolactam)cobalt(II).—Cobalt(II) chloride hexahydrate (1.428 g, 0.006 mole) was dissolved in a minimum quantity of hot 1-butanol. NMTBuL (1.38 g, 0.012 mole) was added and the solution was stirred vigorously. A finely crystalline material formed. After cooling, the product was collected, washed with anhydrous ether, and recrystallized from 1-butanol. It is soluble in most of the common organic solvents. Nitromethane or acetone solutions are fairly stable. However, on prolonged standing of these solutions, there appears to be a slight change in the color.

Dibromobis(N-methyl- γ -thiobutyrolactam)cobalt(II).—The preparation was similar to that described for the chloro complex. Cobalt(II) bromide hexahydrate (1.643 g, 0.005 mole) and NMTBuL (1.15 g, 0.010 mole) were used. This compound has solubility characteristics similar to the chloro complex.

Diiodobis(N-methyl- γ -thiobutyrolactam)cobalt(II).—It was prepared directly from anhydrous cobalt(II) iodide. A hot solution of cobalt(II) salt in butanol was added to the ligand in a mole ratio of 1:2, and the resulting crystalline material was filtered, washed with anhydrous ether, and recrystallized from 1-butanol. Solubility characteristics were similar to the chloro and bromo complexes. However, the stability is somewhat poor.

Dinitratobis(N-methyl- γ -thiobutyrolactam)cobalt(II).—Hydrated cobalt(II) nitrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, was digested with 100% excess of DMP for 2 hr at room temperature. The resulting solution was evaporated almost to dryness. The residue was dissolved in a small quantity of 1-butanol, to which was added NMTBuL dissolved in a minimum quantity of 1-butanol. A crystalline product was formed immediately. The product was recrystallized from isopropyl alcohol, filtered, washed with anhydrous ether, air dried, and stored in a desiccator.

Diethiocyanatobis(N-methyl- γ -thiobutyrolactam)cobalt(II).—The procedure was similar to that described for the nitrate complex. The product does not separate immediately, but the resulting oily, green-blue substance on extended scratching and trituration with ethyl ether affords a crystalline solid. It was recrystallized from isopropyl alcohol, filtered, and washed with anhydrous ether. It is soluble in most of the common organic solvents.

Infrared Spectra.—Infrared spectra were obtained by a Perkin-Elmer Model 521 recording spectrophotometer. Spectra in the 4000–650- cm^{-1} region were obtained by using sodium chloride windows with Nujol mull smears, and in some cases with KBr pellets.

Magnetic Susceptibility Measurements.—The magnetic susceptibilities were determined by the Faraday method. Mercury(II) tetrathiocyanatocobaltate(II) was used as a magnetic susceptibility standard¹⁵ and the diamagnetic corrections were estimated by a procedure outlined by Figgis and Lewis.¹⁶

Electrolytic Conductance Measurements.—Conductance measurements were obtained with an Industrial Instruments Model RC 16B2 bridge and a conventional cell previously calibrated with an aqueous solution of potassium chloride. All measurements were conducted at 25° in nitromethane.¹⁰

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(13) R. Mecke, Jr., and R. Mecke, Sr., *Chem. Ber.*, **89**, 343 (1956).

(14) K. Starke, *J. Inorg. Nucl. Chem.*, **11**, 77 (1959).

(15) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(16) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, p 403.

TABLE I
ANALYTICAL DATA AND OTHER CHARACTERISTIC PROPERTIES OF THE COBALT(II) TBuL AND NMBTuL COMPLEXES

Complex	Color	% yield	Mp, °C	Analyses											
				Theory				Found				Other	Theory	Found	
				C	H	N	Co	C	H	N	Co				
C ₄ H ₇ NS	White	54	112–113	47.52	6.93	13.86	...	47.21	7.17	14.70	
Co(C ₄ H ₇ NS) ₄ (ClO ₄) ₂	Green	96	...	29.03	4.23	8.46	8.90	29.49	4.20	8.65	8.74	ClO ₄	30.03	30.23	
Co(C ₄ H ₇ NS) ₂ Cl ₂	Blue	94	165 dec	28.94	4.22	8.43	17.75	29.71	4.41	8.75	17.65	Cl	21.50	22.24	
Co(C ₄ H ₇ NS) ₂ Br ₂	Azure-blue	97	160	22.82	3.32	6.65	14.01	22.69	3.62	6.77	14.08	S	15.23	14.66	
Co(C ₄ H ₇ NS) ₂ I ₂	Green	87	155	18.66	2.71	5.43	11.42	19.20	3.27	5.76	11.05	S	12.45	12.21	
Co(C ₄ H ₇ NS) ₂ (NO ₃) ₂	Dark blue	64	124–125	24.94	3.68	14.54	15.30	24.83	3.95	14.11	14.92	NO ₃	32.19	32.40	
C ₅ H ₉ NS	White	64	...	52.40	7.83	12.15	...	53.05	8.05	12.10	
Co(C ₅ H ₉ NS) ₄ (ClO ₄) ₂	Green	98	...	33.44	5.01	7.80	8.21	33.19	5.14	7.32	7.86	ClO ₄	27.69	27.29	
Co(C ₅ H ₉ NS) ₂ Cl ₂	Blue	90	152	32.46	4.86	7.57	15.87	32.69	4.85	7.36	15.81	
Co(C ₅ H ₉ NS) ₂ Br ₂	Azure-blue	98	157	26.75	4.01	6.24	13.13	26.72	4.13	6.18	13.13	S	14.28	13.73	
Co(C ₅ H ₉ NS) ₂ I ₂	Green	50	195	22.12	3.32	5.10	10.85	21.69	3.43	5.11	10.64	S	11.81	10.90	
Co(C ₅ H ₉ NS) ₂ (NO ₃) ₂	Purple	~90	100–104	28.98	4.35	13.54	14.26	28.95	4.28	13.55	14.15	NO ₃	30.00	29.74	
Co(C ₅ H ₉ NS) ₂ (SCN) ₂	Blue	~90	83–85	35.56	4.45	13.82	14.54	35.35	4.11	13.37	14.38	

TABLE II
INFRARED SPECTRA, MAGNETIC SUSCEPTIBILITIES, AND ELECTROLYTIC CONDUCTIVITIES IN NITROMETHANE

Compound	Infrared spectra		Magnetic susceptibilities at 300°K			Electrolytic conductance at 25°	
	$\nu(\text{CS})^a$, cm ⁻¹	$\Delta\nu(\text{CS})$, cm ⁻¹	10 ⁶ χ_m	10 ⁶ χ_m^{cor}	μ_{eff} BM	concn $\times 10^3$, M	λ_m , cm ² ohm ⁻¹ mole ⁻¹
C ₄ H ₇ NS (= TBuL)	1112
[Co(TBuL) ₄](ClO ₄) ₂	Masked by ClO ₄	...	9207	9540	4.79	1.12 3.04	163.0 142.0
[Co(TBuL) ₂ Cl ₂]	1098	–14	8748	8936	4.64	1.00 3.06	8.1 4.8
[Co(TBuL) ₂ Br ₂]	1100	–12	8887	9097	4.68	1.02 3.04	9.1 5.0
[Co(TBuL) ₂ I ₂]	1100	–12	8858	9100	4.70	0.98 1.96	20.2 13.4
[Co(TBuL) ₂ (NO ₃) ₂]	1100	–12	7984	8163	4.43	1.04 2.79	16.8 13.4
C ₄ H ₉ NS (= NMTBuL)	1120
[Co(NMTBuL) ₄](ClO ₄) ₂	Masked by ClO ₄	...	9190	9571	4.80	1.00 3.04	183.0 152.0
[Co(NMTBuL) ₂ Cl ₂]	1112	–8	8859	9071	4.68	1.01 3.01	9.5 7.6
[Co(NMTBuL) ₂ Br ₂]	1112	–8	8966	9201	4.71	1.03 3.00	10.3 8.1
[Co(NMTBuL) ₂ I ₂]	1110	–10	9092	9364	4.74	1.00 3.05	12.4 9.2
[Co(NMTBuL) ₂ (NO ₃) ₂]	1110	–10	9380	9583	4.80	1.00 3.03	15.9 11.8
[Co(NMBTuL) ₂ (SCN) ₂]	1110	–10	8914	9142	4.68	1.00 3.33	18.3 12.0

^a The assignment of this frequency to the CS group is not intended to imply that the absorption is due only to the C=S group. Undoubtedly there are significant contributions from the C—N group.

Electronic Absorption Spectra.—The spectra of all complexes in the 350–2200-m μ region were obtained with a Cary Model 14 recording spectrophotometer. Approximately millimolar solutions in nitromethane and acetone were scanned in matched cells of 1-cm light path. Spectra were also obtained on solid compounds in the form of Nujol mulls as described by Lee, *et al.*¹⁷ Computations for Dq , B' , and β were performed on a General Electric Model 235 digital computer.

Results

The analytical data and other characteristic properties of these complexes are summarized in Table I.

The magnetic properties, infrared spectra, and electrical conductivities of these complexes are listed in Table II. The magnetic moments are believed accurate to ± 0.02 BM.

The molar conductance values for these complexes in nitromethane indicate that ion association is obviously occurring, as evidenced by decreasing conductivities at higher concentrations. All halide, nitrate,

(17) R. H. Lee, G. Griswold, and J. Kleinberg, *Inorg. Chem.*, **3**, 1278 (1964).

TABLE III
 SPECTRAL DATA FOR TBuL AND NMTBuL COBALT(II) COMPLEXES

Compound	State	$\nu_3, \text{cm}^{-1} \times 10^{-3} (\epsilon_{\text{max}})$						$\nu_2, \text{cm}^{-1} \times 10^{-3} (\epsilon_{\text{max}})$	
		Assignment							
		4A_2		$^4T_1 (P)$		$^4T_1 (F)$			
[Co(TBuL) ₂ Cl ₂]	Nujol mull	13.89	(...)	14.82	(...)	15.38	(...)	5.59	(...)
	nitromethane	14.16	(441)	15.15	(588)	16.08	(529)	6.01	(87)
	+ 0.02 M TBuL								
[Co(TBuL) ₂ Br ₂]	Nujol mull	13.79	(...)	14.97	(...)	15.87	(...)	5.43	(...)
	nitromethane	13.79	(673)	14.60	(720)	15.58	(579)	5.99	(66)
	+ 0.02 M TBuL								
[Co(TBuL) ₂ I ₂]	Nujol mull	13.16	(...)	13.70	(...)	14.60	(...)	5.38	(...)
	nitromethane	13.12	(900)	13.89	(840)	14.75	(620)	5.83	(105)
	+ 0.02 M TBuL								
[Co(TBuL) ₂ (NO ₃) ₂]	Nujol mull	14.29	(...)	15.75	(...)	...		4.88	(...)
	nitromethane		18.87	(519)	6.90	(29)
	+ 0.02 M TBuL								
[Co(TBuL) ₄](ClO ₄) ₂	Nujol mull	14.74	(...)	15.38	(...)	16.26	(...)	5.68	(...)
	nitromethane	13.98	(760)	14.49	(760)	15.38	(510)	7.04	(155)
	+ 0.02 M TBuL								
[Co(NMTBuL) ₂ Cl ₂]	Nujol mull	13.98	(767)	14.49	(767)	15.74	(505)
	nitromethane	13.97	(...)	15.04	(...)	16.39	(...)	5.75	(...)
	+ 0.02 M NMTBuL	14.49	(379)	15.50	(515)	16.00	(515)	6.08	(76)
[Co(NMTBuL) ₂ Br ₂]	Nujol mull	14.08	(...)	14.45	(...)	15.15	(...)	5.55	(...)
	nitromethane	13.98	(583)	14.75	(750)	15.50	(620)	5.97	(84)
	+ 0.02 M NMTBuL								
[Co(NMTBuL) ₂ I ₂]	Nujol mull	13.24	(...)	13.79	(...)	14.66	(...)	5.52	(...)
	nitromethane	13.42	(1019)	14.08	(990)	14.92	(731)	5.86	(109)
	+ 0.02 M NMTBuL								
[Co(NMTBuL) ₂ (SCN) ₂]	Nujol mull	14.18	(...)	15.67	(...)	17.09	(...)	6.54	(...)
	nitromethane	14.49	(800)	15.62	(830)	16.95	(640)	7.41	(222)
	+ 0.02 M NMTBuL								
[Co(NMTBuL) ₄](ClO ₄) ₂	Nujol mull	14.70	(...)	15.43	(...)	21.74	(...)	5.88	(...)
	nitromethane	14.12	(1360)	14.71	(1300)	15.50	(740)	7.04	(212)
	+ 0.05 M NMTBuL								
	+ 0.10 M NMTBuL	14.12	(1360)	14.71	(1300)	15.50	(740)	...	

and thiocyanate complexes behave as nonelectrolytes in nitromethane. This result suggests that these complexes may be formulated as [Co(TBuL)₂X₂] and [Co(NMTBuL)₂X₂] (X = Cl, Br, I, NO₃, and SCN), which is very typical of the known cobalt(II) complexes containing sulfur donors.^{6,8-10}

The spectral data for the complexes in the solvent nitromethane plus ligand and in the solid state are given in Table III. The values for Dq , B' , and β for complexes are indicated in Table IV. The quantity β is defined as the percentage lowering of the P-F term splitting in the complex compared to the value of that of the gaseous ion with no crystalline field. Spectra of the complexes plus ligand in nitromethane solution are shown in Figures 1 and 2.

Discussion

Elemental analyses of these complexes indicate that the complexes are four-coordinate species. The colors of these complexes are very similar to those of the complexes reported for other sulfur donors.^{6,8-10} On the basis of color, it could be assumed that these complexes also possess a tetrahedral geometry.

However, the oxygen-containing analogs of TBuL and NMTBuL with cobalt(II) perchlorate yield octahedral configurations.^{18,19} This tendency toward

(18) S. K. Madan and J. Sturr, unpublished work.

(19) R. J. Niedzielski and G. Zinder, *Can. J. Chem.*, **43**, 2618 (1965).

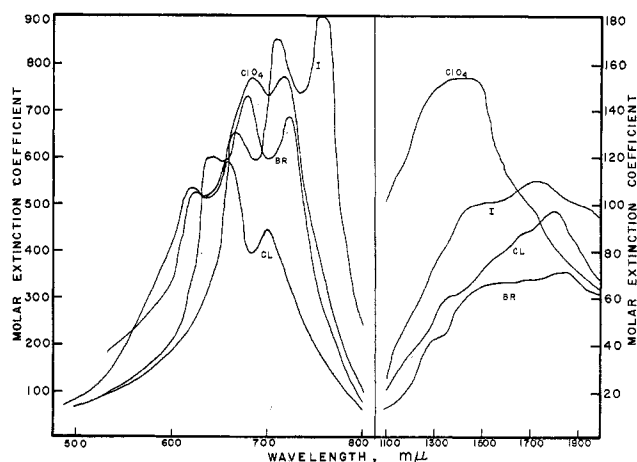


Figure 1.—Spectra of cobalt(II) complexes of TBuL plus 0.02 M TBuL in nitromethane.

change in coordination number from six to four in the corresponding thiolactam complexes [Co(TBuL)₄](ClO₄)₂ and [Co(NMTBuL)₄](ClO₄)₂ may be explained on the basis of π -bonding interaction between the sulfur and metal atoms.^{20,21}

(20) E. Eisenberg, J. A. Ibers, R. J. H. Clark, and H. G. Gray, *J. Am. Chem. Soc.*, **86**, 113 (1964); A. R. Latham, V. C. Hascall, and H. B. Gray, *Inorg. Chem.*, **4**, 788 (1965).

(21) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *ibid.*, **85**, 3049 (1963).

TABLE IV

SUMMARY OF SPECTRAL ASSIGNMENTS AND DERIVED ELECTRONIC STRUCTURE
PARAMETERS FOR THE TETRAHEDRAL COBALT(II) COMPLEXES

Complex	State	ν_2 , cm^{-1}	ν_3 , cm^{-1}	Dq , cm^{-1}	B' , cm^{-1}	β
[Co(TBuL) ₂ Cl ₂]	Nujol mull	5580	14,660	320	708	0.73
	nitromethane	6000	15,150	345	719	0.74
	+ 0.02 M TBuL					
[Co(TBuL) ₂ Br ₂]	Nujol mull	5430	14,450	312	702	0.72
	nitromethane	5990	14,700	345	697	0.71
	+ 0.02 M TBuL					
[Co(TBuL) ₂ I ₂]	Nujol mull	5380	13,700	309	653	0.67
	nitromethane	5830	13,790	338	631	0.65
	+ 0.02 M TBuL					
[Co(TBuL) ₂ (NO ₃) ₂]	Nujol mull	4880	15,040	278	772	0.79
	nitromethane	6900	18,870	393	929	0.95
	+ 0.02 M TBuL					
[Co(TBuL) ₄](ClO ₄) ₂	Nujol mull	5680	14,880	326	718	0.71
	nitromethane	7040	14,710	412	626	0.64
	+ 0.02 M TBuL					
[Co(NMTBuL) ₂ Cl ₂]	Nujol mull	5750	14,970	330	721	0.73
	nitromethane	6080	15,430	350	735	0.75
	+ 0.02 M NMTBuL					
[Co(NMTBuL) ₂ Br ₂]	Nujol mull	5560	14,450	319	696	0.71
	nitromethane	5970	14,810	344	698	0.71
	+ 0.02 M NMTBuL					
[Co(NMTBuL) ₂ I ₂]	Nujol mull	5520	13,790	318	652	0.67
	nitromethane	5860	13,990	338	646	0.66
	+ 0.02 M NMTBuL					
[Co(NMTBuL) ₂ (SCN) ₂]	Nujol mull	6540	15,340	378	702	0.71
	nitromethane	7410	15,380	434	652	0.66
	+ 0.02 M NMTBuL					
[Co(NMTBuL) ₄](ClO ₄) ₂	Nujol mull	5880	14,880	338	707	0.72
	nitromethane	7040	14,920	411	642	0.65
	+ 0.05 M NMTBuL					

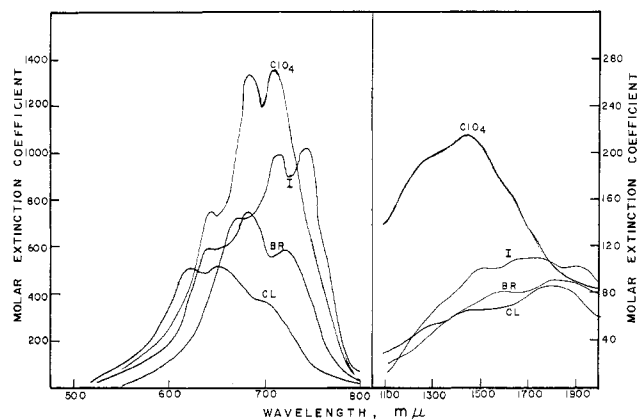


Figure 2.—Spectra of cobalt(II) complexes of NMTBuL plus 0.02 M NMTBuL in nitromethane.

Infrared Spectra.—Evidence for coordination through the sulfur donor site can be found by examining the infrared spectra. The infrared spectrum of TBuL has been reported by Mecke and Mecke.¹³ These workers have attributed the characteristic frequencies at 1110, 1290, 3000, 1533, and 784 cm^{-1} to the $\nu(\text{CS})$, $\nu(\text{CN})$, $\nu(\text{NH})$, $\delta(\text{NH})$, and $\gamma(\text{NH})$, respectively. Since coordination was believed to take place through the sulfur atom of the CS group, this frequency was studied. The CN stretch was also examined. Table II gives a summary of the changes in thiocarbonyl stretching frequency upon coordination of the TBuL and NMTBuL with the metal ion. The shift of the

CS stretch in all cases is in the direction of lower frequency and longer wavelength. This is indicative of bond weakening and decrease in double-bond character of CS with electron density being drawn away by interaction with the metal ion. This in itself is evidence for the use of sulfur donor sites.

The bands observed in the 3- μ region for TBuL are obviously assigned to the N-H stretching vibrations. The bands are somewhat sharper in the spectra of the complexes than in the TBuL. This suggests that hydrogen bonding is not present in these coordination compounds.

Magnetic and Conductance Measurements.—In Table II are listed the magnetic properties of these complexes. The magnetic moments of these complexes are within the range expected for spin-free, tetrahedral complexes.²² The value of 4.80 BM for [Co(NMTBuL)₂(NO₃)₂], a purple crystalline compound, rather slightly unstable in organic solvents such as acetone and nitromethane, indicates that this complex may have two different forms, depending upon the state of the complex. A value of 4.80 BM was obtained for tetrakis(N-methyl- γ -thiobutyrolactam)cobalt(II) perchlorate. The predicted moment for tetrahedral cobalt(II) complexes is usually lower than the value found. Even though the measured magnetic moment is not far from the predicted value for cobalt(II) in a tetrahedral field, an assign-

(22) F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961).

ment of the structure of the compound on this basis alone would not be justified.

The conductance measurements in nitromethane are also given in Table II. The conductance data of solutions of these complexes in nitromethane are in agreement with reference values of $177 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ for 2:1 complexes with $5\text{--}30 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ for nonelectrolytes, given by Gill and Nyholm.²³ The data for $[\text{Co}(\text{TBuL})_4](\text{ClO}_4)_2$, $[\text{Co}(\text{NMTBuL})_4](\text{ClO}_4)_2$, $[\text{Co}(\text{TBuL})_2\text{X}_2]$, and $[\text{Co}(\text{NMTBuL})_2\text{X}_2]$ (where X = Cl, Br, I, NO_3 , and SCN) indicate that these complexes are four-coordinate and probably tetrahedral.

Electronic Absorption Spectra.—The spectra were obtained using nitromethane plus ligand and Nujol mulls. For these compounds a comparison of the spectra in nitromethane and Nujol mulls indicates the primary absorbing species in solution is the same as in the solid state. However, the spectral data and conductance measurements suggest that these complexes in solution appear to be slightly solvolyzed. The solution spectra were taken to ascertain the molar extinction coefficients. The molar extinction coefficients shown in Table III fall within the acceptable values for tetrahedral cobalt(II) species. Assignments of the electronic transitions for the observed bands for most of these complexes were made on the basis of tetrahedral symmetry. Assignments of the electronic transitions for the observed bands for $[\text{Co}(\text{NMTBuL})_2(\text{NO}_3)_2]$ were made on the basis of octahedral symmetry. Using the secular equation of Tanabe and Sugano²⁴ and the procedure outlined by Cotton,²² we obtained the spectral parameters Dq , B' , and β , which are summarized in Table IV. All of these quantities are in the usual ranges expected for tetrahedral Co(II) complexes.

The results recorded in Tables III and IV for the $[\text{Co}(\text{TBuL})_4](\text{ClO}_4)_2$ and $[\text{Co}(\text{NMTBuL})_4](\text{ClO}_4)_2$ complexes indicate they possess the tetrahedral stereochemistry, similar to the complexes reported for other sulfur-containing ligands.^{6,8-10} However, these complexes in solution are unstable; they tend to be solvolyzed or otherwise decomposed. Similar behavior is reported for the $[\text{Co}(\text{thiourea})_4]^{2+}$ and $[\text{Co}(\epsilon\text{-thiocaprolactam})_4]^{2+}$, but by the addition of excess of thiourea the $[\text{Co}(\text{thiourea})_4]^{2+}$ ion is stabilized.⁹ Therefore, to obtain spectra of the species $[\text{Co}(\text{TBuL})_4]^{2+}$ and $[\text{Co}(\text{NMTBuL})_4]^{2+}$ in nitromethane, known amounts of TBuL and NMTBuL were added to reach a limiting spectra, Table III. The absorption band and molar extinction coefficients for these complexes occur at the values expected of tetrahedral Co(II) stereochemistry.

The spectral parameters determined for TBuL and NMTBuL (Table IV) as ligands enable us to assign each a position relative to other recently investigated sulfur-containing donors in the spectrochemical series for cobalt(II) in a tetrahedral field.^{6,8-10} The following Dq values show the position in the series of TBuL

and NMTBuL with respect to other sulfur-containing donors: γ -thiobutyrolactam (326)⁷ < sulfide (330)²⁵ < N-methyl- γ -thiobutyrolactam (338)⁷ < N,N-dimethylthioacetamide (387)¹⁰ < ϵ -thiocaprolactam (391)⁶ < thiourea (425).⁹

Using the Dq and B' values for $[\text{CoX}_4]^{2-}$ (X = Cl, Br, I, and SCN),²² together with those for $[\text{Co}(\text{TBuL})_4]^{2+}$ and $[\text{Co}(\text{NMTBuL})_4]^{2+}$ and adopting the average ligand field approximation, it is possible to calculate the Dq and B' values for the $[\text{Co}(\text{TBuL})_2\text{X}_2]$ and $[\text{Co}(\text{NMTBuL})_2\text{X}_2]$ complexes (X as indicated above). The comparison between the observed and calculated values is illustrated in Table V. The calculated values of Dq for $[\text{Co}(\text{TBuL})_2\text{I}_2]$, $[\text{Co}(\text{NMTBuL})_2\text{I}_2]$, and $[\text{Co}(\text{NMTBuL})_2(\text{SCN})_2]$ are 292–298, 299–304, and 396 cm^{-1} , respectively. The observed values of Dq for $[\text{Co}(\text{TBuL})_2\text{I}_2]$ and $[\text{Co}(\text{NMTBuL})_2\text{I}_2]$ are 17–11 and 19–14 cm^{-1} greater than the calculated values, and the observed value for $[\text{Co}(\text{NMTBuL})_2(\text{SCN})_2]$ is 18 cm^{-1} less than the calculated value. This is more than the uncertainty associated with any individual Dq value. We attribute this discrepancy to poor stability of these complexes.

TABLE V
COMPARISON OF OBSERVED AND CALCULATED
AVERAGE LIGAND FIELD

Compound	Observed		Calculated	
	Dq , cm^{-1}	B' , cm^{-1}	Dq , cm^{-1}	B' , cm^{-1}
$[\text{Co}(\text{TBuL})_2\text{Cl}_2]$	321	709	312–327	704–724
$[\text{Co}(\text{TBuL})_2\text{Br}_2]$	311	702	302–308	694–719
$[\text{Co}(\text{TBuL})_2\text{I}_2]$	309	653	292–298	694–704
$[\text{Co}(\text{NMTBuL})_2\text{Cl}_2]$	330	721	319–333	699–719
$[\text{Co}(\text{NMTBuL})_2\text{Br}_2]$	319	696	309–315	689–714
$[\text{Co}(\text{NMTBuL})_2\text{I}_2]$	318	652	299–304	674–699
$[\text{Co}(\text{NMTBuL})_2(\text{SCN})_2]$	378	708	396	699

An examination of the Dq parameters in the spectrochemical series for ϵ -thiocaprolactam and TBuL allows us to assign a donor order based on ring size. The Dq values for the cobalt(II) complexes in a tetrahedral field for these thiolactams suggest a donor order of five-membered < seven-membered ring. A similar donor order based on ring size for nickel(II) complexes in an octahedral field for the corresponding oxygen-containing analogs of the thiolactams has also been observed.⁴

The Dq parameters for five-membered substituted and unsubstituted thiolactam complexes of cobalt(II), in a tetrahedral field, exhibit no evidence of a steric effect, which has been shown to exist for the corresponding five-membered substituted and unsubstituted lactam complexes of nickel(II), in an octahedral field.⁴ The Dq values of nickel(II) complexes for the N-methylactams were significantly lower than those for the unsubstituted compounds. The variation in the Dq parameter was rationalized on the basis of steric effect.⁴ However, for cobalt(II) complexes, the Dq parameter for the five-membered substituted thiolactam (338 cm^{-1}) is larger than that of the five-membered

(23) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 997 (1959).

(24) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753 (1954).

(25) R. Pappalardo and R. E. Dietz, *Phys. Rev.*, **123**, 1188 (1961).

TABLE VI
 INFRARED BANDS PERTINENT TO THE STATE OF THE NITRATE ION IN $\text{Co}(\text{TBuL})_2(\text{NO}_3)_2$ AND $\text{Co}(\text{NMTBuL})_2(\text{NO}_3)_2$

Observed bands, cm^{-1}		Assignment	Accepted bands, cm^{-1} ³¹		
$\text{Co}(\text{TBuL})_2(\text{NO}_3)_2$	$\text{Co}(\text{NMTBuL})_2(\text{NO}_3)_2$		$\text{Ni}(\text{en})_3(\text{NO}_3)_2$, ionic NO_3	$\text{Ni}(\text{en})_2(\text{NO}_3)_2$, monodentate NO_3	$\text{Ni}(\text{en})_2\text{NO}_3(\text{ClO}_4)_2$, bidentate NO_3
815 m, sp	810 m, sp	ν_2	823 m, sp	818 m, sp	809 m, sp
1300 s	1275 m, sp	ν_3	1368 vs, br	1307 s	1290 w, sp
1405 s	1425 m, sp			1420 s	1475 w, sp
720 w, br	705 w	ν_4	704 w, sp	708 w, sp	695 vw
755 w, br	747 w			728 w, sp	746 w, sp

^a s, strong; m, medium; w, weak; v, very; br, broad; sp, sharp.

 TABLE VII
 NEAR-INFRARED AND VISIBLE SPECTRA OF $[\text{Co}(\text{NMTBuL})_2(\text{NO}_3)_2]$

Compound	State	$\nu_1, \text{cm}^{-1} \times 10^{-3}$ (ϵ_{max})	$\nu_2, \text{cm}^{-1} \times 10^{-3}$ (ϵ_{max})	$\nu_3, \text{cm}^{-1} \times 10^{-3}$ (ϵ_{max})
Assignment				
$^4\text{T}_{1g}(\text{F})$				
$[\text{Co}(\text{NMTBuL})_2(\text{NO}_3)_2]$	Nitromethane	7.69 (39)	$^4\text{A}_{2g}(\text{F})$	$^4\text{T}_{1g}(\text{P})$
	Nitromethane + 0.02 M NMTBuL	6.99 (38)	...	18.87 (125)
	Nujol mull	7.19 (...)	15.87 (...)	17.54 (261)
				18.18 (...)

unsubstituted thiolactam (326 cm^{-1}). The reversal in the trend may be explained on the basis of symmetry. Since these complexes have been shown to possess a tetrahedral configuration, it is reasonable to assume that the methyl groups of the adjacent ligands coordinated to the metal ion are far apart, so that there arises no steric repulsion between the coordinated ligands. However, this is not so for nickel(II) octahedral environment.⁴ Besides the symmetry consideration, another contribution that plays a significant role in the donor strength and increase in the Dq parameter for NMTBuL is the inductive effect, as the methyl group is electron releasing. Inductive effects have been previously detected as a function of the Dq parameter for some amides.³

The Nitrate Complexes.—The infrared spectra of $\text{Co}(\text{TBuL})_2(\text{NO}_3)_2$ and $\text{Co}(\text{NMTBuL})_2(\text{NO}_3)_2$ were investigated to obtain evidence for ionic or coordinated nitrate ion. The infrared spectrum of coordinated nitrate ion has previously been described.^{26–30} Curtis³¹ has recently reported that the nitrate ion in ionic compounds exhibits three bands: ν_2 (out-of-plane deformation), ν_3 (doubly degenerate stretch), and ν_4 (doubly degenerate in-plane bending). When the nitrate ion is coordinated as a monodentate or a bidentate ligand, all bands become active, shifts in band positions and intensities are observed, and the degeneracy of ν_3 and ν_4 is lifted. For a coordinated monodentate nitrate ion, ν_3 is weakened and there is splitting of ν_3 and ν_4 and a small shift of ν_2 to lower frequency. However, for a coordinated bidentate nitrate ion, an enhancement

of the above modes is noticed. Table VI shows the infrared spectra of the nitrate complexes, along with the model compounds in which an ionic, monodentate, and bidentate nitrate ion is present.³¹

The infrared spectra of $\text{Co}(\text{TBuL})_2(\text{NO}_3)_2$ and $\text{Co}(\text{NMTBuL})_2(\text{NO}_3)_2$ provide evidence that these complexes contain a monodentate and bidentate nitrate ion, respectively. However, the analytical data and conductance measurements indicate that these complexes may be formulated as $[\text{Co}(\text{TBuL})_2(\text{NO}_3)_2]$ and $[\text{Co}(\text{NMTBuL})_2(\text{NO}_3)_2]$, both being four-coordinate species.

The solution spectrum of $\text{Co}(\text{TBuL})_2(\text{NO}_3)_2$ in various solvents is difficult to obtain, as in each case examined there appears to be a color change, indicative of decomposition or solvolysis. However, a limiting spectrum was obtained by adding 0.02 M TBuL to the nitromethane solution of this complex. A ϵ_{max} value of $519 \text{ M}^{-1} \text{ cm}^{-1}$ observed for this spectrum agrees with the expected range for a tetrahedral species, but the spectral parameters listed in Table IV for this species exhibit very poor agreement. Apparently, the electronic spectrum of the solid sample is quite similar to that of the $[\text{Co}(\text{TBuL})_4](\text{ClO}_4)_2$, even though it imparts no information on band intensities. We believe that the spectrum in the solid state is consistent with a tetrahedral $\text{Co}(\text{II})$ stereochemistry, whereas the solution spectrum is more typical of octahedral cobalt(II) or a mixture of both of the species. Further, the magnetic moment of 4.43 BM seems to fit well with the postulation of tetrahedral configuration in the solid state, thus supporting the spectral data.

The magnetic and spectral measurements, on the contrary, indicate that $[\text{Co}(\text{NMTBuL})_2(\text{NO}_3)_2]$ has cobalt(II) in an octahedral field. The near-infrared and visible spectrum of $[\text{Co}(\text{NMTBuL})_2(\text{NO}_3)_2]$, shown in Figure 3 and recorded in Table VII, is substantially different from the spectra of the other complexes of this series. The spectrum is not characteristic of tetrahedral cobalt(II), but instead is more typical of

(26) S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chem.*, **3**, 480 (1964).

(27) B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, 4222 (1957); *J. Inorg. Nucl. Chem.*, **8**, 75 (1958).

(28) C. C. Addison and B. M. Gatehouse, *J. Chem. Soc.*, 613 (1960); B. M. Gatehouse and A. E. Counyns, *ibid.*, 3965 (1958).

(29) E. P. Bertin, R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **81**, 3818 (1959).

(30) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963; E. Bannister and F. A. Cotton, *J. Chem. Soc.*, 2276 (1960).

(31) N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, **4**, 804 (1965).

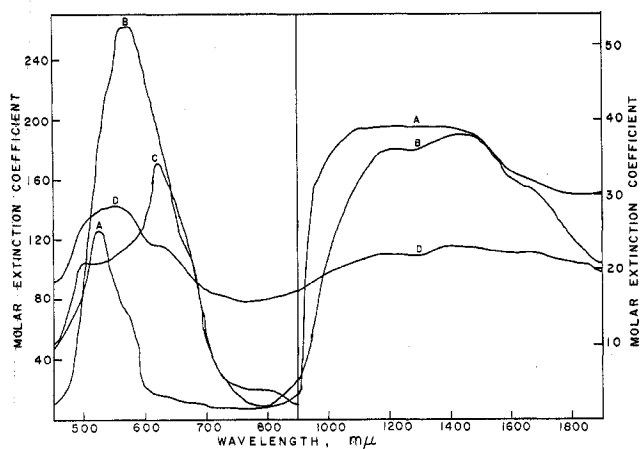


Figure 3.—Spectra of $[\text{Co}(\text{NMTBuL})_2(\text{NO}_3)_2]$: (A) in nitromethane; (B) in nitromethane + 0.02 *M* NMTBuL; (C) reflectance spectrum (absorbance, arbitrary units); (D) Nujol mull spectrum (absorbance, arbitrary units).

octahedrally coordinated cobalt(II) ion. The spectrum of this compound in nitromethane is characterized by an ϵ_{max} value of $125 \text{ M}^{-1} \text{ cm}^{-1}$, which is slightly higher than the expected value for octahedral species. This observation could be interpreted in terms of solvolysis of the $[\text{Co}(\text{NMTBuL})_2(\text{NO}_3)_2]$ to $[\text{Co}$

average of two or three species. Therefore, it is not unreasonable to assume that the observed ϵ_{max} value fits better for an octahedral stereochemistry. The magnetic susceptibility of 4.80 BM in the solid state is just at the range expected for octahedral coordination and further supports the spectral measurements.

The electronic spectrum of this complex may be interpreted in terms of the crystal field treatment of the quartet states of the cobalt(II) ion in an octahedral field, ignoring ${}^4\text{T}_{1g}(\text{F})$ – ${}^4\text{T}_{1g}(\text{P})$ interactions. The energies of the four quartet states are written as follows:⁹ ${}^4\text{T}_{1g}(\text{P})$, $12B$; ${}^4\text{A}_{2g}$, $12Dq$; ${}^4\text{T}_{2g}$, $2Dq$; ${}^4\text{T}_{1g}(\text{F})$, $-6Dq$. If the absorption band observed at 7194 cm^{-1} (ν_1) is identified with the transition ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, the strong absorption band in the $18,182\text{-cm}^{-1}$ (ν_3) region may be assigned to ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ transitions. For $[\text{Co}(\text{NMTBuL})_2(\text{NO}_3)_2]$ the value of Dq calculated is only approximate, since the measurement of the ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ transition was rather difficult. This peak could not be resolved but showed up as a broad shoulder on the $18,182\text{-cm}^{-1}$ peak. Using the estimated value for Dq and the secular equation³² the $E(\text{P}) - E(\text{F})$ energy, B' , and β were calculated (Table VIII).

On the basis of the evidence of magnetic moment,

TABLE VIII
LIGAND FIELD PARAMETERS^a OF THE NMTBuL COBALT(II) OCTAHEDRAL COMPLEX

Compound	Phase	Dq, cm^{-1}	$E(\text{P}) - E(\text{F}), \text{cm}^{-1}$	B'^b	β
$[\text{Co}(\text{NMTBuL})_2(\text{NO}_3)_2]$	Nitromethane	876	12,179	812	0.83
	Nitromethane + 0.02 <i>M</i> NMTBuL	804	11,499	767	0.78
	Nujol mull	821	11,679	779	0.80

^a Estimated. ^b $B' = E(\text{P}) - E(\text{F})/15$.

$(\text{NMTBuL})_2\text{NO}_3\text{S}]^+$ or $[\text{Co}(\text{NMTBuL})_2\text{S}_2]^{2+}$ ions (S = solvent molecule). These ions may possess a tetrahedral character. Since ϵ_{max} values for the tetrahedral Co(II) are usually higher, it is quite probable that the slightly higher value of observed ϵ_{max} is actually the

electronic spectra, and infrared spectra, it is reasonable to suggest that the nitrate ligand is bidentate in this complex.³¹

(32) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 256.