

Cobalt(III), Nickel(II), and Copper(II) Complexes of 1-Thia (or Oxa)-4,7-diazacyclononane and Related Mixed-Ligand Cobalt(III) Complexes

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Summary

To investigate the effect of substitution of an oxygen or a sulphur donor atom for a nitrogen donor atom in a cyclic triamine, 1,4,7-triazacyclononane (tacn), cobalt(III), nickel(II), and copper(II) complexes of 1-oxa-4,7-diazacyclononane (taon) and 1-thia-4,7-diazacyclononane (tasn), and related mixed ligand cobalt(III) complexes were prepared and characterized. The coordination ability of an ether-oxygen or a thioether-sulphur atom increases when these atoms are incorporated into cyclic terdentate ligands. Electronic spectra reveal that ligand field strengths of these atoms are enhanced significantly. The presence of these heteroatoms affects circular dichroism spectra because of the increased flexibility of the chelate rings.

Introduction

Complexes of cyclic triamines are being studied actively^(1–3). However, relatively little work has been done on these complexes as compared with the extensive investigations on complexes of cyclic quadridentate ligands⁽⁴⁾. Further studies on complexes of cyclic terdentate ligands are necessary to elucidate the characteristics of these ligands. We have been interested in transition metal complexes of cyclic triamines⁽⁵⁾ and now extend our study to complexes of cyclic terdentate ligands containing an oxygen or sulphur donor atom. In this

paper cobalt(III), nickel(II), and copper(II) complexes of 1-oxa-4,7-diazacyclononane (abbreviated as taon) and 1-thia-4,7-diazacyclononane (tasn) are reported. In the text, 1,4,7-triazacyclononane is abbreviated as tacn, (R)-2-methyl-1,4,7-triazacyclononane as mtcn, and (R)-5-methyl-1-oxa-4,7-diazacyclononane as mton.

Results and Discussion

The colours of the three nickel(II) complexes, [NiL₂]²⁺ (L = tacn⁽⁵⁾, tasn or taon) range from reddish purple to bluish purple, while those of the copper ones change from blue to bluish violet in the order of the ligands⁽⁶⁾. This is shown quantitatively by the electronic spectra (Nujol mulls) in the solid state (Figure 1). The spectra of the solid nickel complexes are

Table 1. Analytical results for the ligands and complexes.

Compound	Found (Calcd.) %		
	C	H	N
taon · 2 HCl	35.4(35.5)	8.1(7.9)	13.8(13.8)
tasn · H ₂ SO ₄ · 0.5 H ₂ O	28.3(28.4)	6.7(6.8)	11.1(11.1)
A [Ni(taon) ₂](ClO ₄) ₂	27.6(27.8)	5.4(5.5)	10.8(10.8)
B [Ni(mton) ₂](PF ₆) ₂	26.7(26.4)	5.1(5.1)	9.0(8.8)
C [Ni(tasn) ₂](ClO ₄) ₂	26.4(26.2)	5.1(5.1)	10.2(10.2)
D [Cu(taon) ₂](ClO ₄) ₂	27.4(27.6)	5.4(5.4)	10.6(10.7)
E [Cu(mton) ₂](ClO ₄) ₂	30.5(30.5)	5.8(5.9)	10.3(10.2)
F [Cu(tasn) ₂](ClO ₄) ₂	25.7(26.0)	5.2(5.1)	10.0(10.1)
G [Co(tacn)(taon)]Cl ₃ · 4.5 H ₂ O	28.2(28.5)	7.4(7.6)	13.8(13.9)
H-1 [Co(mtcn)(taon)]Cl ₃ · 4.5 H ₂ O	29.9(30.0)	7.2(7.8)	13.4(13.5)
H-2	29.9	7.8	13.6
H-3	30.1	7.5	13.5
H-4	29.5	7.8	13.4
H-5	29.5	7.2	13.2
I [Co(tacn)(tasn)]Cl ₃ · 3 H ₂ O	28.8(29.1)	7.0(7.1)	14.1(14.2)
J-1 [Co(mtcn)(tasn)]Cl ₃ · 4.5 H ₂ O	29.1(29.1)	7.3(7.5)	13.2(13.1)
J-2	29.1	7.5	13.0
J-3	28.9	7.7	13.0
J-4	28.7	7.8	12.9
K [Co(tasn) ₂]Cl ₃ · 4.5 H ₂ O	26.9(26.8)	7.0(6.9)	10.4(10.4)

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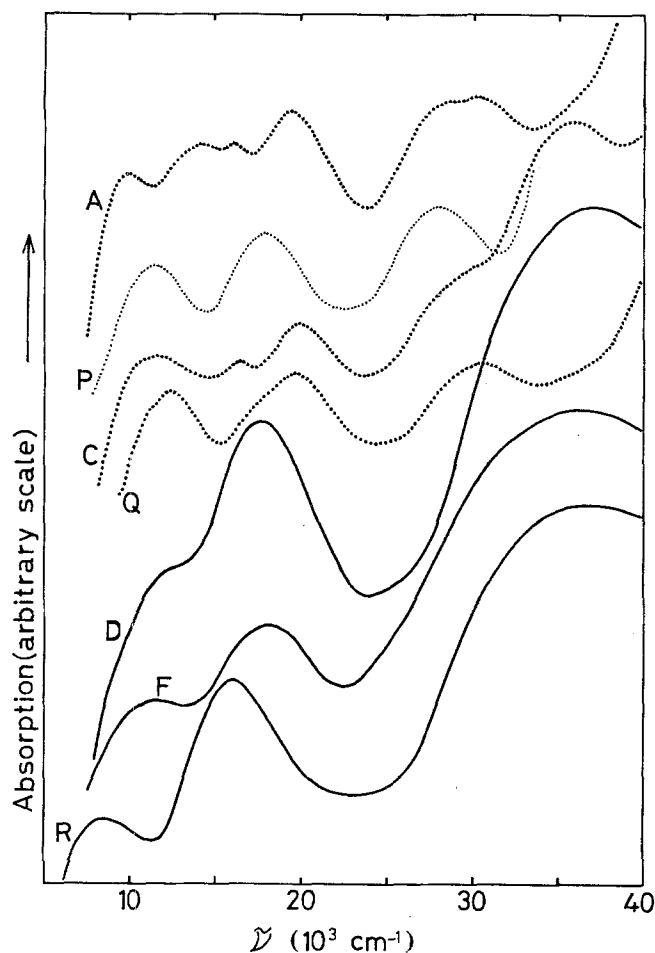
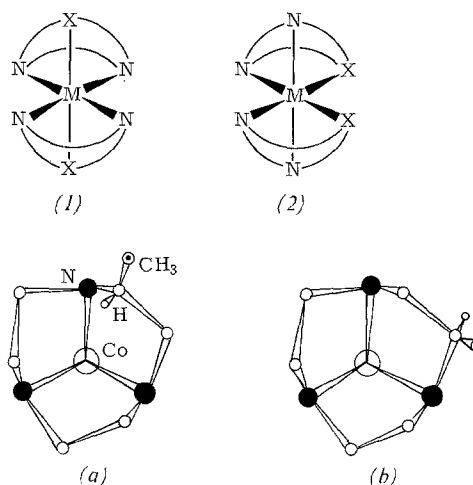


Figure 1. Electronic spectra of solid complexes (Nujol mulls): A, [Ni(taon)₂](ClO₄)₂; C, [Ni(tasn)₂](ClO₄)₂; D, [Cu(taon)₂](ClO₄)₂; F, [Cu(tasn)₂](ClO₄)₂; P, [Ni(daes)₂](ClO₄)₂; Q, [Ni(tacn)₂](ClO₄)₂; and R, [Cu(tacn)₂](ClO₄)₂.

quite different from the absorption spectra reported for their aqueous solutions⁽⁷⁻⁹⁾, which are explained in terms of an approximately octahedral ligand field. In the case of the copper complexes the solid spectra are, however, similar to those of the aqueous solutions (Table 2).

The electronic spectrum of solid $[\text{Ni}(\text{tacn})_2](\text{ClO}_4)_2$ (Figure 1 Q) shows three slightly irregularly shaped bands: $\nu_1(^3A_{2g} \rightarrow ^3T_{2g})$, $\nu_2[\rightarrow ^3T_{1g}(\text{F})]$, and $\nu_3[\rightarrow ^3T_{1g}(\text{P})]$, but that of $[\text{Ni}(\text{tasn})_2](\text{ClO}_4)_2$ has one additional peak between broad, distorted bands assigned to ν_1 and ν_2 . The spectrum is nearly identical to that of $[\text{Ni}(\text{tasn})_2](\text{NO}_3)_2$ (the structure of which was determined by x-ray to have a *trans*-S configuration, structure (1)⁽⁸⁾) and is very different from that of *cis*-S- $[\text{Ni}(\text{daes})_2](\text{ClO}_4)_2$ (Figure 1 P; daes = bis(2-aminoethyl)sulphide⁽¹⁰⁾). The spectrum of $[\text{Ni}(\text{taon})_2](\text{ClO}_4)_2$ is quite different from the above.

The substitution of a sulphur or an oxygen donor for one nitrogen donor of tacn lowers the symmetry of the ligand. This causes splitting of energy levels of the complexes. The spectrum of solid $[\text{Ni}(\text{taon})_2](\text{ClO}_4)_2$ (Figure 1 A) can be explained on the assumption of an approximate D_{4h} symmetry ligand



field. Six transitions are expected: $^3B_{1g} \rightarrow ^3E_g$, $\rightarrow ^3B_{2g}$, $\rightarrow ^3A_{2g}(\text{F})$, $\rightarrow ^3E_g(\text{F})$, $\rightarrow ^3A_{2g}(\text{P})$, and $\rightarrow ^3E_g(\text{P})$ in the order of an increasing energy⁽¹¹⁾. The fifth transition $[\rightarrow ^3A_{2g}(\text{P})]$ is

Table 2. Absorption and circular dichroism spectra of the complexes in aqueous solutions.

Complex		Absorption $\nu_{\text{max}}/10^3 \text{ cm}^{-1} (\log \epsilon)$		Circular dichroism $\nu_{\text{ext}}/10^3 \text{ cm}^{-1} (\Delta \epsilon)$	
B	$[\text{Ni}(\text{mton})_2](\text{PF}_6)_2$	11.4(0.78)	18.7(0.99)	11.8(0.62)	12.3sh(+)
		27.9(0.91)	30.0sh	16.0(0.064)	18.8(-0.020)
		48.9(3.76)		21.3(0.0024)	27.1(-0.019)
D	$[\text{Cu}(\text{taon})_2](\text{ClO}_4)_2$	13.0sh	18.0(1.71)		
		38.1(3.79)			
E	$[\text{Cu}(\text{mton})_2](\text{ClO}_4)_2$	13.0sh	17.8(1.74)	12.4(0.042)	18.1(0.93)
		37.7(3.82)		34.3(0.93)	43.8(4.08)
F	$[\text{Cu}(\text{tasn})_2](\text{ClO}_4)_2$	10.8(1.06)	17.9(1.72)		
		37.0(3.75)			
G	$[\text{Co}(\text{tacn})(\text{taon})]\text{Cl}_3 \cdot 4.5 \text{ H}_2\text{O}$	21.4(1.89)	29.5(1.90)		
		43.5(4.28)			
H-1	$[\text{Co}(\text{mtcn})(\text{taon})]\text{Cl}_3 \cdot 4.5 \text{ H}_2\text{O}$	21.2(1.88)	29.4(1.91)	21.1(4.14)	29.3(-0.79)
		43.2(4.29)		43.8(15.5)	
H-2		21.3(1.92)	29.4(1.94)	21.2(3.98)	29.3(-0.86)
		43.2(4.31)		43.6(13.5)	
H-3		21.2(1.92)	29.4(1.92)	21.0(3.90)	29.3(-0.81)
		43.2(4.31)		43.3(14.5)	
H-4		21.2(1.88)	29.4(1.91)	21.1(3.91)	29.4(-0.73)
		43.2(4.29)		43.6(15.3)	
H-5		21.2(1.88)	29.4(1.92)	21.0(3.96)	29.3(-0.76)
		43.2(4.30)		43.8(15.6)	
I	$[\text{Co}(\text{tacn})(\text{tasn})]\text{Cl}_3 \cdot 3 \text{ H}_2\text{O}$	21.3(2.05)	29.2(2.14)		
		36.2(3.95)	43.3(4.20)		
J-1	$[\text{Co}(\text{mtcn})(\text{tasn})]\text{Cl}_3 \cdot 4.5 \text{ H}_2\text{O}$	21.3(2.10)	29.2(2.18)	21.4(4.04)	28.8(-0.98)
		36.4(3.98)	43.1(4.23)	36.5sh(+)	43.7(16.9)
J-2		21.2(2.11)	29.1(2.18)	21.4(3.58)	28.8(-0.91)
		36.2(3.98)	43.1(4.23)	36.5sh(+)	43.4(15.7)
J-3		21.2(2.11)	29.1(2.19)	21.4(3.42)	28.7(-0.89)
		36.1(3.99)	43.0(4.24)	36.5sh(+)	43.2(15.5)
J-4		21.2(2.08)	29.3(2.20)	21.3(3.22)	28.8(-0.74)
		36.0(3.98)	43.1(4.23)	36.5sh(+)	43.6(16.8)
K	$[\text{Co}(\text{tasn})_2]\text{Cl}_3 \cdot 4.5 \text{ H}_2\text{O}$	20.9(2.13)	ca. 27sh		
		35.0(4.12)	42.4(4.12)		

assigned to a shoulder at $28.5 \times 10^3 \text{ cm}^{-1}$. The large splitting of $\nu_1(^3A_{2g} \rightarrow ^3T_{2g})$ should be due to the distinct difference in ligand field strengths between ether 1-O and amino-N donors. In the case of $[\text{Ni}(\text{tasn})_2](\text{ClO}_4)_2$ (Figure 1 C) the first two transitions are not well separated, and are incorporated in an envelope of the broad distorted, lowest energy band. In an aqueous solution the absorption spectrum of $[\text{Ni}(\text{tasn})_2]^{2+}$ reported⁽⁸⁾ is very similar to the spectrum of solid *cis*-S- $[\text{Ni}(\text{daes})_2](\text{ClO}_4)_2$. The structures of $[\text{NiL}_2]^{2+}$ (L = tasn or taon) in aqueous solutions should be altered from those of the solid states, although Hancock *et al.*⁽⁸⁾ have presumed a *trans*-S configuration for $[\text{Ni}(\text{tasn})_2]^{2+}$ in aqueous solution.

The electronic spectra of the solid copper complexes show one main peak in the visible region with an additional peak or shoulder of the lower-energy side of the main peak (Figure 1). The separation between the two decreases in the order of the ligands: tacn, tasn, taon. The i.r. spectra of the copper complexes are nearly superimposable on those of the corresponding nickel ones, suggesting that the copper complexes have also a *trans*-X configuration (I) in the solid state. In addition the absence of a strong sulphur-to-copper charge-transfer band in the near ultraviolet region is consistent with the fact that sulphur is not coordinated in an equatorial plane⁽¹²⁾. Based on a tetragonal chromophore⁽¹¹⁾, *trans*- $[\text{Cu}_4\text{X}_2]$ (X = N, S or O), the lower energy, X-sensitive bands are assigned to the transition $d_{z^2} \rightarrow d_{x^2-y^2}$, while the higher energy main bands may be composed of the transitions, d_{xy} and/or d_{yz} , $d_{zx} \rightarrow d_{x^2-y^2}$. The energy difference between the d_{z^2} orbital and the d_{xy} and/or d_{yz} , d_{zx} orbitals is shown to increase in the order of X: O, S, N, the order in which bonding between X and the d_{z^2} orbital is presumed to increase.

In the expectation that circular dichroism (CD) spectra would give more information about the electronic properties of metal ions, we attempted to prepare the optically active ligand, mton, from (R)-1,2-propanediamine, but the yield was extremely low. Without characterization of the ligand, it was

used to prepare the nickel(II) and copper(II) complexes (Table 1). The absorption spectra are almost identical to those of the corresponding taon complexes. The CD spectra are given in Figure 2 and Table 2. Corresponding to the absorption spectrum, $[\text{Cu}(\text{mton})_2](\text{ClO}_4)_2$ shows two CD limits in the ligand-field-transition region. The CD limit of the main band is only slightly less than that of $[\text{Cu}(\text{mtcn})_2](\text{ClO}_4)_2$. The chelate rings of the two ligands, mtcn and mton, may have a similar chiral conformation.

The electronic spectra of $[\text{Ni}(\text{tasn})_2]^{2+}$ and $[\text{Ni}(\text{taon})_2]^{2+}$ in aqueous solutions have been explained on the basis of an octahedral ligand field but that of $[\text{Ni}(\text{tacn})_2]^{2+}$ has been analyzed on assumption of a D_{3d} ligand field⁽¹³⁾. The spectral patterns of $[\text{Ni}(\text{tacn})_2]^{2+}$ and $[\text{Ni}(\text{taon})_2]^{2+}$ are, respectively, very similar to those of the optically active $[\text{Ni}(\text{mtcn})_2]^{2+}$ and $[\text{Ni}(\text{mton})_2]^{2+}$. The CD spectrum of $[\text{Ni}(\text{mtcn})_2]^{2+}$ reported previously suggests that the symmetry of the ligand field is lower than octahedral and is consistent with the spectral analysis⁽¹³⁾ for $[\text{Ni}(\text{tacn})_2]^{2+}$. The CD spectrum of $[\text{Ni}(\text{mton})_2]^{2+}$ differs slightly, but clearly shows the splittings of the three d-d transitions expected from an O_h symmetry. The low symmetry results in the unusual Racah parameter B value (1100 cm^{-1}) reported for $[\text{Ni}(\text{tasn})_2]^{2+}$ based on an O_h approximation⁽¹⁰⁾.

The CD limit corresponding to the allowed transition $^3A_{2g} \rightarrow ^3T_{2g}$ of $[\text{Ni}(\text{mton})_2]^{2+}$ is nearly half the value of $[\text{Ni}(\text{mtcn})_2]^{2+}$ ($\Delta\epsilon = 1.21$). A nickel-oxygen (ether) bond is usually weaker than a nickel-nitrogen (amine) bond. This results in a more flexible conformation of the chelate rings of mton and then chirality of the rings may be diminished. In contrast to the nickel complex, the corresponding copper mton complex has only a slightly smaller value compared to that of the mtcn one. This may be due to the fact that $[\text{Cu}(\text{mtcn})_2]^{2+}$ is already distorted tetragonally, like tetragonal $[\text{Cu}(\text{mton})_2]^{2+}$.

The cobalt(III) complexes in Table 1 were obtained, but so far the attempt to isolate $[\text{Co}(\text{taon})_2]^{3+}$ is unsuccessful. To trace the origins, formal reduction potentials of some of the complexes were estimated from cyclic voltammetry (the voltammograms reveal that the processes are quasi-reversible): -634 mV vs. SCE for $[\text{Co}(\text{tacn})_2]^{3+}$; -427 for $[\text{Co}(\text{tacn})(\text{tasn})]^{3+}$; -302 for $[\text{Co}(\text{tasn})_2]^{3+}$; -227 for $[\text{Co}(\text{tacn})(\text{taon})]^{3+}$. These results suggest that $[\text{Co}(\text{taon})_2]^{3+}$ reduces easily, which makes isolation difficult.

The cobalt(III) complexes are yellow or yellow-orange, including $[\text{CoL}(\text{taon})]^{3+}$ (L = tacn and mtcn) which possesses a chromophore $[\text{CoN}_5\text{O}]^{3+}$, for which reddish colours like those of $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ and $[\text{Co}(\text{NH}_3)_5(\text{MeOH})]^{3+}$ are expected. Electronic spectral data are given in Table 2. Red shifts of the d-d transitions are found upon substitution of an oxygen or a sulphur atom for a nitrogen atom of one of the two tacn ligands. The shifts of the first band $^1A_{1g} \rightarrow ^1T_{1g}$ (in an O_h approximation; $\nu_{\text{max}} = 21.78 \times 10^3 \text{ cm}^{-1}$ for $[\text{Co}(\text{tacn})_2]^{3+}$) are as follows: $0.40 \times 10^3 \text{ cm}^{-1}$ for $[\text{Co}(\text{tacn})(\text{taon})]^{3+}$; 0.50×10^3 for $[\text{Co}(\text{tacn})(\text{tasn})]^{3+}$; (disubstitution) 0.86×10^3 for $[\text{Co}(\text{tasn})_2]^{3+}$. The corresponding red shifts are larger for substitution of X for NH_3 of $[\text{Co}(\text{NH}_3)_6]^{3+}$ ($\nu_{\text{max}} = 21.01 \times 10^3 \text{ cm}^{-1}$): 0.68×10^3 for X = H_2O ; 0.97×10^3 for MeOH; 1.4×10^3 for S_2O_3 ; 1.48×10^3 for SCN. These facts imply that the ligand field strengths of oxygen and sulphur atoms when one of the donor atoms of the cyclic ligands are appreciably enhanced compared with the strengths when they are monodentate as in H_2O , MeOH, S_2O_3 , and SCN. Upon compression of the cyclic structure, the hetero-atoms of taon and tasn are arranged in a suitable position for coordination and produce relatively strong ligand fields.

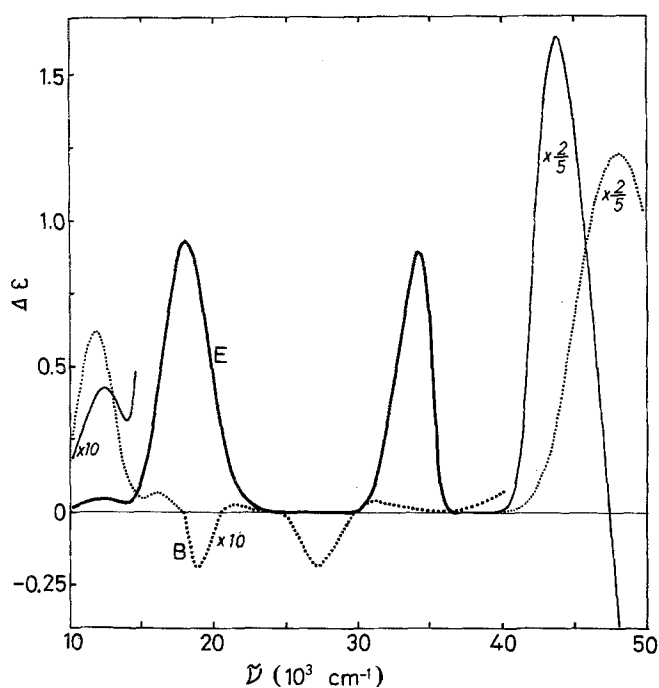


Figure 2. CD spectra of aqueous solutions: B, $[\text{Ni}(\text{mton})_2](\text{PF}_6)_2$ and E, $[\text{Cu}(\text{mton})_2](\text{ClO}_4)_2$.

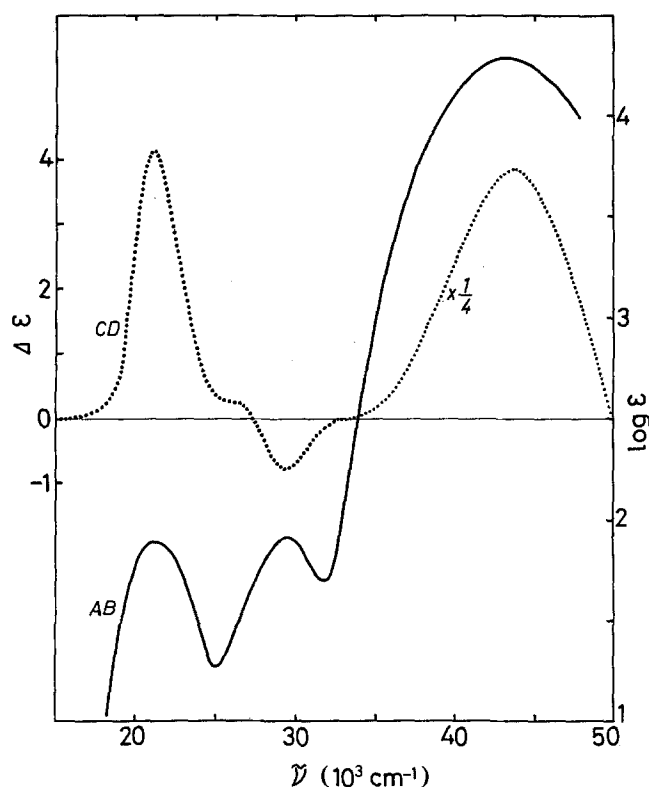


Figure 3. Absorption (AB) and circular dichroism (CD) spectra of H-1 $[\text{Co}(\text{mtcn})(\text{taon})]\text{Cl}_3 \cdot 4.5\text{H}_2\text{O}$ in aqueous solution.

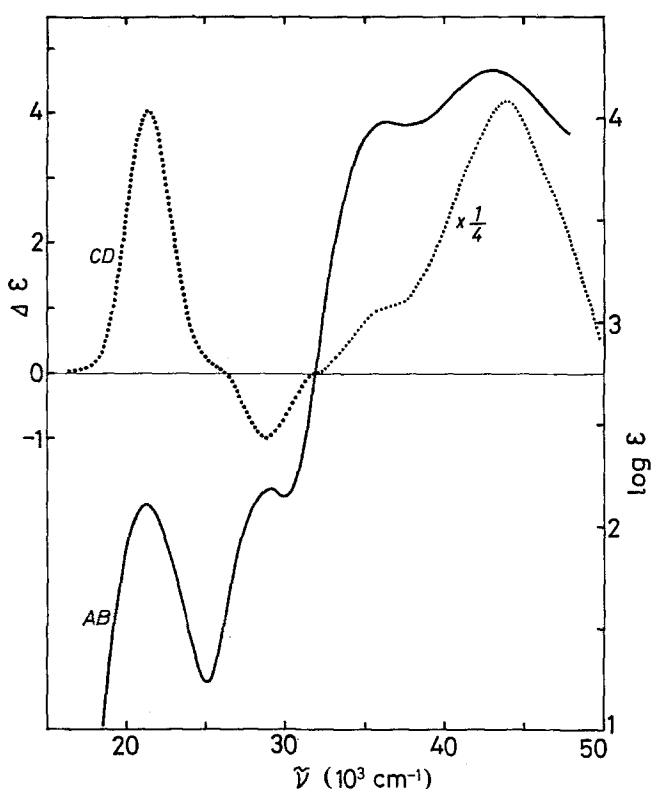


Figure 4. Absorption (AB) and circular dichroism (CD) spectra of J-1 $[\text{Co}(\text{mtcn})(\text{tasn})]\text{Cl}_3 \cdot 4.5\text{H}_2\text{O}$ in aqueous solution.

In the near u.v. region, $[\text{Co}(\text{tacn})(\text{tasn})]^{3+}$ shows a band at $36.2 \times 10^3 \text{ cm}^{-1}$, which is absent in the spectrum of $[\text{Co}(\text{tacn})(\text{taon})]^{3+}$ (the spectral patterns are almost identical to those of the corresponding mtcn complexes shown in Figures 3 and 4). The band is assigned to a sulphur-to-cobalt charge-transfer transition. The intensity is enhanced in the spectrum of $[\text{Co}(\text{tasn})_2]^{3+}$ where two sulphur atoms are coordinated to the cobalt atom.

Two isomers with *trans*-S and *cis*-S configurations [(1) and (2)] are possible for $[\text{Co}(\text{tasn})_2]^{3+}$ but Sargeson *et al.*⁽¹⁴⁾ have reported only the *cis*. The ^{13}C n.m.r. spectrum of the complex (in D_2O , at 15 MHz) shows nine peaks (at 35.95, 38.35, 39.16, 50.72, 53.36, 54.05, 55.43, and 56.08 ppm) and the individual intensity of the weaker three (at 38.35, 53.56, and 56.08 ppm) is nearly half the individual intensity of the stronger six. Consideration of their symmetries reveals that three ^{13}C signals are expected for the *trans*-S isomer (1) and six signals for the *cis* (2). In an aqueous solution the complex should be a mixture of *trans*-S and *cis*-S isomers (the ratio *cis*-S/*trans*-S = 4/1). All attempts to separate the isomers have been unsuccessful so far.

The effect of the presence of an oxygen or sulphur atom in cyclic tridentate ligands upon CD spectra were examined and the data are given in Table 2 and Figures 3 and 4. The optically active ligand, mtcn, produces two modes of coordinations *a* and *b*, and for the mixed ligand complexes, $[\text{Co}(\text{mtcn})(\text{tasn})]^{3+}$ and $[\text{Co}(\text{mtcn})(\text{taon})]^{3+}$, six isomers are possible because of relative dispositions of the methyl substituent of mtcn and the sulphur or oxygen atom of tasn or taon. Partial separation of the isomers was obtained by SP Sephadex C-25 column chromatography⁽¹⁵⁾ with an aqueous 0.2 M disodium hydrogen phosphate as eluent (Table 1).

The complexes $[\text{Co}(\text{mtcn})(\text{taon})]^{3+}$ and $[\text{Co}(\text{mtcn})(\text{tasn})]^{3+}$ are separated into five and four bands, respectively. The ^1H n.m.r. spectra show that the third band (H-3) of the former complex contains two isomers and both the third (J-3) and the fourth (J-4) bands of the latter also contain two isomers. The other bands contain a single isomer. Based on the chemical shifts of the methyl group of mtcn, the two coordination modes *a* and *b* have previously been assigned to isomers of mtcn complexes (*a* and *b*). For example, for $[\text{Co}(\text{mtcn})(\text{tacn})]^{3+}$ the chemical shift of mtcn coordinated in the mode *a* is at 1.52 ppm and that in the mode *b* at 1.36 ppm. The presence of oxygen or sulphur donors disturbs this criterion because the chemical shifts are then changed to a considerable degree.

The absorption spectra and CD patterns of comparable isomers of $[\text{Co}(\text{mtcn})(\text{taon})]^{3+}$ and $[\text{Co}(\text{tacn})(\text{tasn})]^{3+}$ are similar, while slight differences in the intensities of CD limits are observed among the isomers. The CD intensities of the transition, $^1A_1 \rightarrow ^1E$, of $[\text{Co}(\text{mtcn})(\text{taon})]^{3+}$ are comparable to those of $[\text{Co}(\text{mtcn})(\text{tacn})]^{3+}$ (isomer *a*, $\nu_{\text{ext}} = 21.2 \times 10^3 \text{ cm}^{-1}$ ($\Delta\epsilon = 4.06$) and isomer *b*, $21.1 \times 10^3 \text{ cm}^{-1}$, 3.98) showing that the chelate rings of $[\text{Co}(\text{mtcn})(\text{taon})]^{3+}$ are restricted to a λ conformation like those of $[\text{Co}(\text{mtcn})(\text{tacn})]^{3+}$ where one chiral centre of mtcn restricts the chirality of all or nearly all the chelate rings to λ ⁽⁵⁾. Some differences in CD intensities ($^1A_1 \rightarrow ^1E$) were observed among the isomers of $[\text{Co}(\text{mtcn})(\text{tasn})]^{3+}$ and the lower intensities suggest that the chelate rings are less constrained to a λ conformation. Longer C-S and Co-S bonds compared to C-O and C-N, and to Co-O and Co-N, respectively, increase the flexibility of chelate rings and then decrease the portion of chelate rings with a λ conformation. This results in the lower CD intensities.

Experimental

Measurements

Measurements were carried out by the methods reported previously⁽⁵⁾. Cyclic voltammograms were recorded with a Yanagimoto P-1100 Polarographic Analyzer equipped with the standard three electrode cell at a scan of 50 mV/s. The working electrode was of glassy carbon and solutions were ca. 10⁻³ M in sample and 0.1 M in supporting electrolyte (LiClO₄). Potentials were recorded vs. SCE at room temperature and E_{1/2} values were taken as the average of the anodic and cathodic peak potentials. The analytical results are given in Table 1.

Synthesis of the ligands

The cyclic triamines, tacn·3HCl and mtcn·3HCl, were prepared by the literature methods⁽⁵⁾. The ditosylates of tasn and taon were prepared by the known procedures^(7, 8) and detosylated by using concentrated sulphuric acid ten times the weight of the ditosylates at 100–110°C for several hours. During the hydrolysis, a few drops of the reaction mixture were occasionally removed and mixed with a small amount of water, and when they had dissolved completely, the heating was stopped. To the reaction mixture cooled to room temperature was carefully added with stirring sufficient ether to precipitate a dark brown mass, which was isolated from the mother liquor by decantation. The crude product was dissolved in hot water, treated with active charcoal, and the filtrate was concentrated to a small volume, to which was added sufficient ethanol. Crystals of tasn·H₂SO₄·0.5H₂O were obtained in a yield of 52%, m.p. 220–222°C, but the sulphate of taon did not crystallize. The latter was converted to the hydrochloride, taon·2HCl, m.p. 187–189°C (in a yield of 59%). The ligand mton was synthesized similarly as above but in a very low yield (less than 5%). Therefore, the crude sulphate precipitated by ether from the hydrolyzed mixture was used directly to prepare the complexes without characterization.

Synthesis of the complexes

Nickel(II) and copper(II) complexes

An aqueous solution of metal chloride (1 mmol) and ligand salt (2 mmol) was neutralized with an aqueous solution of lithium hydroxide and the mixture was filtered after heating for ca. 30 min on a steam bath. To the filtrate was added lithium perchlorate (3 mmol) or sodium hexafluorophosphate and it was concentrated to a small volume on a steam bath to crystallize the product. The product was recrystallized from water and dried in air.

Cobalt(III) complexes

Preparation of [Co(tasn)₂]³⁺ was reported in the literature⁽¹⁴⁾ but the complex was isolated as the chloride in this study.

The mixed ligand complexes were prepared from the ligand salt and [CoCl₃L] (L = tacn and mtcn)⁽⁵⁾. To a solution prepared from the ligand salt (1 mmol) and DBU (1,8-diazabicyc-

lo[5.4.0]undec-7-ene) (2 mmol) in dimethylsulfoxide (10 cm³) was added the solid trichloro-complex and the mixture was heated on a steam bath with occasional stirring for a few hours until the solid had disappeared. The cooled mixture was diluted with water, and chromatographed on an SP Sephadex C-25 column (3 cm Ø × 150 cm) with 0.2 M aqueous disodium hydrogen phosphate as eluent. In the case of [Co(tacn)-(taon)]³⁺ and [Co(tacn)(tasn)]³⁺ a single yellow orange band was obtained, from which the chloride was isolated in the usual procedure⁽¹⁵⁾. For [Co(mtcn)(taon)]³⁺ five bands (ratio: 22, 12, 38, 19, 9) were obtained and assigned as H-1, H-2, H-3, H-4, and H-5, respectively, in the order of elution. The first band (H-1) was completely separated from the second (H-2), which was partially overlapping with the third (H-3). The separation of the bands (H-4) and (H-5) was also insufficient. Four bands, assigned as J-1, J-2, J-3, and J-4 (formation ratio: 25, 16, 34, 25) were identified for [Co(mtcn)(tasn)]³⁺ but the bands (J-2) and (J-3) were poorly separated. The overlapping portions of these bands were subjected to repeated chromatography. These complexes were all isolated as the chlorides. The chemical shift of the methyl group of mtcn of each band (at 60 MHz, in 2% DCl-D₂O vs. DSS): for [Co(mtcn)(taon)]³⁺, H-1, δ = 1.50 ppm; H-2, 1.39 ppm; H-3, 1.42 and 1.28; H-4, 1.60; H-5, 1.44, and for [Co(mtcn)(tasn)]³⁺, J-1, 1.48; J-2, 1.35; J-3, 1.31 and 1.46; J-4, 1.54 and 1.64 ppm.

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References

- (1) K. Wieghardt, W. Schmidt, W. Herrmann and H.-J. Küppers, *Inorg. Chem.*, 22, 2953 (1983) and refs. therein.
- (2) K. Wieghardt, M. Hahn, W. Swiridoff and J. Weiss, *Inorg. Chem.*, 23, 94 (1984).
- (3) K. Wieghardt, K. Pohl and W. Gebert, *Angew. Chem.*, 95, 739 (1983).
- (4) G. A. Melson (Ed.), in *Coordination Chemistry of Macrocyclic Compounds*, Plenum Press, New York, 1979.
- (5) M. Nonoyama and K. Sakai, *Inorg. Chim. Acta*, 72, 57 (1983) and refs. therein.
- (6) Room temperature magnetic moments, μ_{eff}: [Ni(taon)₂](ClO₄)₂, 3.09; [Ni(tasn)₂](ClO₄)₂, 3.03; [Cu(taon)₂](ClO₄)₂, 1.83; [Cu(tasn)₂](ClO₄)₂, 1.84 μ_B.
- (7) R. D. Hancock and V. J. Thöm, *J. Am. Chem. Soc.*, 104, 291 (1982).
- (8) S. M. Hart, J. C. A. Boeyens, J. P. Michael and R. D. Hancock, *J. Chem. Soc., Dalton Trans.*, 1601 (1983).
- (9) In Ref. (8), the third band ³A_{2g} → ³T_{1g}(P) was reported to be obscured by charge-transfer transitions, but we observed the band at 30.0 × 10³ cm⁻¹ (log ε = 0.97). Sulphur-to-nickel charge-transfer bands were observed at 36.6 sh and 38.2(3.61).
- (10) S. M. Hart, J. C. A. Boeyens and R. D. Hancock, *Inorg. Chem.*, 22, 982 (1983).
- (11) A. B. P. Lever, *Coord. Chem. Rev.*, 3, 119 (1968).
- (12) O. Yamauchi, H. Seki and T. Shoda, *Bull. Chem. Soc. Jpn*, 56, 3258 (1983).
- (13) J. S. Alper and L. J. Zompa, *J. Inorg. Nucl. Chem.*, 42, 1693 (1980).
- (14) L. R. Gahan, G. A. Lawrance and A. M. Sargeson, *Aust. J. Chem.*, 35, 119 (1982).
- (15) Y. Yoshikawa and K. Yamasaki, *Coord. Chem. Rev.*, 28, 205 (1979).

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TMC 1141