THE PARAMAGNETISM OF NICKEL COMPLEXES OF DITHIOOXAMIDE AND ITS DERIVATIVES

C. R. KANEKAR* and A. T. CASEY
Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria 3052 Australia

Abstract—The magnetic susceptibility of nickel complexes of dithiooxamide and of three of its derivatives has been measured over the temperature range 90–300°K. Data are presented for a number of preparations of each compound. The magnitude of the susceptibility is explained on the assumption that the (presumed) polymeric structure consists of both planar and octahedral conformations about the nickel atoms.

INTRODUCTION

DITHIOOXAMIDE and its derivatives have attracted attention as complexing agents for the past 40 yr. A descriptive account of the complexes formed between a number of metals and dithiooxamide and six of its derivatives as well as references to the earlier work has been given by Ray and Xavier[1]. Much of the subsequent work has dealt with analytical applications, especially spectro-photometric estimation of various transition metals[2–10]. Relatively few papers have dealt with the structure of the metal complexes themselves. Jensen[11] suggested, from the properties of diamagnetic four co-ordinate nickel mercaptides which were known to be polymeric, that dithiooxamidonickel(II) would also be polymeric. Barcelo[12] attempted to infer the structure of copper and nickel complexes from the known crystal structure of the ligand[13] and some i.r. measurements. Hurd *et al.*[14, 15] have extended the i.r. observations and imply that they support the structure advanced by Barcelo. They also report surprisingly that dimethyldithiooxamidonickel(II) is paramagnetic with an effective moment

*Present address: Tata Institute of Fundamental Research, Coloba, Bombay 5, India.
1. P. Ray and J. Xavier, *J. Indian chem. Soc.* **38**, 535 (1961).
2. H. W. Baker and R. T. Pflaum, *Proc. Iowa Acad. Sci.* **68**, 174 (1961).
3. W. D. Jacobs and J. H. Yoe, *Analytica. chim. Acta* **20**, 332, 435 (1959).
4. W. D. Jacobs and J. H. Yoe, *Talanta* **2**, 270 (1959).
5. W. D. Jacobs, *Analyt. Chem.* **32**, 512, 514 (1960).
6. W. D. Jacobs, *Analyt. Chem.* **33**, 1279 (1961).
7. W. D. Jacobs, C. M. Wheeler and W. H. Waggoner, *Talanta* **9**, 243 (1962).
8. J. T. Pyle and W. D. Jacobs, *Talanta* **9**, 761 (1962).
9. A. Paul, *Analyt. Chem.* **35**, 211 (1963).
10. W. Wawrzyczek and H. Majkowska, *Z. analyt. Chem.* **199**, 430 (1964).
11. K. A. Jensen, *Z. anorg. allg. Chem.* **252**, 227 (1944).
12. J. Barcelo, *Spectrochim. Acta* **10**, 245 (1958).
13. B. Long, P. Markey and P. G. Wheatley, *Acta Crystallogr.* **7**, 140 (1954).
14. R. N. Hurd, G. DeLaMater, G. C. McElheny and L. V. Peiffer, *J. Am. chem. Soc.* **82**, 4454 (1960).
15. R. N. Hurd, G. DeLaMater, G. C. McElheny and J. P. McDermott, *Advances in the Chemistry of the Co-ordination Compounds* (Edited by S. Kirschner), p. 350. McMillan, New York (1961).

of 2·4 B.M. and imply other complexes of nickel are diamagnetic. Jensen also reports that dithiooxamido Ni(II) is diamagnetic.

These measurements were made at room temperature only. The low magnetic moment obtained by Hurd *et al.* was ascribed to a tetrahedral configuration. However, no tetrahedral structures are known at present involving co-ordination through sulphur atoms. Here are reported a more complete series of results of the magnetic susceptibility of nickel(II) complexes of dithiooxamide and its derivatives.

EXPERIMENTAL

Preliminary studies and other work[14] made it apparent that the composition of the compounds and the magnetic moment depended on the conditions of preparation. Thus a number of preparations of each of the complexes were obtained as follows:

(1) Dithiooxamidonickel (II)

A solution of nickel acetate tetrahydrate (4·25 g, 0·017 mole) in ethanol (400 ml) was added slowly to a well stirred solution of dithiooxamide (2·55 g, 0·021 mole) in ethanol (300 ml). An immediate purple-brown precipitate formed. The liberated acid was neutralized with (A) sodium acetate to pH 4·3; (B) NaOH to pH 4·3; (C) NaOH to pH 8·6; (D) NH_3 to pH 8·1. The ionic strength in each case was adjusted to a constant value of 0·12 with $NaNO_3$. The compounds were extracted in a soxhlet with water and with ethanol to remove soluble impurities, and oven-dried at 110°C. Analytical results* are summarised in Table 1.

(II) N,N'-dimethyldithiooxamidonickel (II)

Preparation A. A solution of nickel acetate tetrahydrate (3·63 g, 0·015 mole) in ethanol (300 ml) was added to a well stirred solution of N,N'-dimethyldithiooxamide (2·7 g, 0·018 mole) in ethanol (400 ml). An immediate purple-brown precipitate formed; the pH was adjusted to 8·1 with NH_3, the precipitate filtered and extracted with a soxhlet as before. Preparation B used nickel nitrate hexahydrate in alcohol and preparation C used acetone as a solvent. Analytical results are in Table 1.

(III) N,N'-bis(hydroxyethyl)dithiooxamidonickel(II)

A solution of nickel acetate tetrahydrate (2·82 g, 0·011 mole) in ethanol (300 ml) was added to a well stirred solution of N,N'-bis (hydroxyethyl)dithiooxamide (2·96 g, 0·016 mole) in ethanol (300 ml). A purple-brown precipitate formed immediately. The pH was adjusted to 8·0 with ammonia and the precipitate filtered and extracted with a soxhlet as before. Preparation B used nickel nitrate hexahydrate in alcohol and preparation C used acetone as solvent. Analytical results are in Table 1.

(IV) N,N'-bis(carboxymethyl)dithiooxamidonickel(II)

Preparation A. A solution of nickel acetate tetrahydrate (2·58 g, 0·011 mole) in ethanol (300 ml) was added to a well-stirred solution of N,N'-bis(carboxymethyl)dithiooxamide (3·00 g, 0·013 mole) in ethanol (300 ml). An orange-brown to grey-brown precipitate formed immediately. The pH was adjusted to 8·0 with ammonia, the solution refluxed for a ½ hr and the compound filtered. Preparation B used acetone as a solvent. Analytical results are summarised in Table 1.

Magnetic measurements were made in the temperature range 90–300°K with a conventional Guoy type balance, using $Hg[Co(NCS)_4]$ as calibrant. The temperatures, measured with a copper-constantan thermocouple, are believed to be accurate at least to 0·5°. The field strength was about 8000 oersted.

Correction for the diamagnetism of the constituent atoms except nickel was made in each case.

*Analyses for carbon, hydrogen, nitrogen and sulphur were carried out by the Australian Micro-analytical Service, C.S.I.R.O. and University of Melbourne. Nickel was estimated by standard methods.

Table 1. Analytical data for nickel complexes of dithiooxamide and derivatives

		Analysis									
		C		H		N		S		Ni	
		Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
I	A	$C_2H_2N_2S_2Ni \cdot H_2O$	13·00	12·26	2·14	2·06	14·64	14·30	33·27	32·73	29·20	29·97
	B	$C_2H_2N_2S_2Ni \cdot H_2O$	11·57	12·26	2·26	2·06	12·40	14·30	29·68	32·73	30·80	29·97
	C	$C_2H_2N_2S_2Ni \cdot H_2O$	11·37	12·26	1·86	2·06	12·31	14·30	31·73	32·73	30·70	29·97
	D	$C_2H_2N_2S_2Ni$	13·55	13·58	1·07	1·14		15·84	34·35	36·25	32·06	33·19
II	A	$C_4H_6N_2S_2Ni \cdot 2H_2O$	17·88	19·93	3·14	4·18	9·72	11·63	24·33	26·61	26·6	24·36
	B	$C_4H_6N_2S_2Ni$	24·23	23·44	3·89	2·95	13·35	13·67	29·72	31·29	28·96	28·65
	C	$C_4H_6N_2S_2Ni$	24·26	23·44	3·60	2·95	13·19	13·67	30·51	31·29	27·84	28·65
	D	$C_4H_6N_2S_2Ni$	23·48	23·44	3·33	2·95	13·66	13·67	30·62	31·29	28·17	28·65
III	A	$C_6H_{10}N_2S_2O_2Ni \cdot H_2O$	25·31	25·47	4·06	4·27	9·23	9·90	22·68	22·66	20·60	20·75
	B	$C_6H_{10}N_2S_2O_2Ni \cdot H_2O$	26·14	25·47	4·22	4·27	8·59	9·90	22·79	22·66	20·60	20·75
	C	$C_6H_{10}N_2S_2O_2Ni \cdot H_2O$	25·12	25·47	4·64	4·27	9·07	9·90	22·65	22·66	20·70	20·75
IV	A	$C_6H_4N_2S_2O_4Ni_2 \cdot 3H_2O$	17·35	17·84	3·30	2·49	7·89	6·94	15·90	15·88	26·82	29·09
	B	$C_6H_4N_2S_2O_4Ni_2$	21·15	20·61	2·80	1·15	9·05	8·01	17·94	18·34	31·26	33·58
	C	$C_6H_4N_2S_2O_4Ni_2$	21·09	20·61	2·50	1·15	8·92	8·01	17·37	18·34	30·28	33·58
	D	$C_6H_4N_2S_2O_4Ni_2$	20·42	20·61	2·68	1·15	8·76	8·01	17·67	18·34	32·80	33·58
	E	$C_6H_4N_2S_2O_4Ni_2$	20·51	20·61	2·74	1·15	9·05	8·01	19·00	18·34	32·04	33·58

RESULTS AND DISCUSSION

(1) Dithiooxamidonickel(II)

The analytical results for the various preparations are shown in Table 1. It is clear that the composition of the compound depends to some extent on the method of preparation. Even duplicate preparations by the same method at the same time show some variation in composition and in magnetic behaviour. These observations are similar to those made by Hurd *et al.* on N,N′-dimethyldithiooxamide nickel. The nickel to ligand ratio differs only slightly from unity in all samples indicating that, if a polynuclear chain is present, it must be fairly long.

For the parent dithiooxamidonickel compound Hurd *et al.*[15] suggested a polymer of fifteen units fitted their analytical data: $(DTO)[(DTO-2H)Ni]_{15}$ where DTO stands for the protonated ligand. The analysis of sample *IA*, prepared using sodium acetate to neutralise the liberated acid, is in agreement with this formula if it is taken to be a dihydrate but we question whether it is fruitful to assign polymer numbers on the basis of analysis alone, when the change in analytical data is so slight. The compound was too insoluble to measure the molecular weight by usual methods.

Magnetic susceptibilities were measured for seven preparations of this complex. Table 2 shows some data for typical samples. The Curie Law appears to be obeyed fairly well, although the susceptibilities observed at higher tempera-

Table 2. Variation of magnetic moments with temperature

Compound		Temp. (°K)	$10^6\chi_M$ (corr)	μ_{eff} B.M.
Dithiooxamidonickel(II) A		90·5	1831	1·15
		250·4	590	1·09
		294	540	1·13
		314	498	1·23
	D	91	2331	1·31
		251·5	831	1·30
		298	715	1·31
		322	632	1·28
		385·5	586	1·35
N,N′-dimethyl-dithiooxamidonickel(II) A		89·5	6502	2·17
		146	3743	2·10
		193	2815	2·09
		251	2209	2·09
		295	1756	2·05
		361	1560	2·13
		388	1442	2·15
	C	94·2	7060	2·32
		137·2	4957	2·34
		184·8	3651	2·33
		234·2	2912	2·35
		290·8	2296	2·32
		334·5	1927	2·28

Table 2. (Contd.)

Compound		Temp. (°K)	$10^6 \chi_M$ (corr)	μ_{eff} B.M.
N,N'-bis(hydroxyethyl) dithiooxamidonickel(II)	A	89	4993	1·89
		146·5	3121	1·92
		248	1964	1·98
		293	1623	1·96
		327	1500	1·99
		388	1326	2·04
	C	95·8	4763	1·92
		117·9	3830	1·91
		153·2	3066	1·95
		209	2333	1·98
		242·3	2029	1·99
		290·2	1727	2·01
N,N'-bis(carboxymethyl) dithiooxamidonickel(II)	A	94	5513	2·04
		146	3574	2·05
		249·5	2256	2·13
		294	1815	2·07
		323	1699	2·07
	B	94·6	7565	2·40
		118·2	6420	2·47
		181	4694	2·62
		250·5	3737	2·75
		264·2	3541	2·75
		291·5	3275	2·78
	C	96·2	5244	2·02
		103	4893	2·02
		165	3651	2·20
		230·5	2920	2·33
		290·5	2352	2·35
		335·6	2078	2·37

tures deviate systematically from those observed at lower temperatures. Part of this may be due to the increasing relative importance of the temperature independent paramagnetism terms, but this ($\sim 60 \times 10^{-6}$) is not sufficient to explain the whole deviation.

The effective magnetic moment of this compound ranges from 1·1 to 1·3 B.M., a value considerabley smaller than that expected 2·9 to 3·1 B.M. for two unpaired spins with spin-orbit coupling. The paramagnetism has been attributed by Hurd et al.[14] to a mixture of planar and tetrahedral conformations, but it is apparent that this explanation cannot be correct. The magnetic behaviour of nickel(II) ion in both weak as well as strong tetrahedral field has been discussed theoretically by Figgis[16, 17]. In both cases, the $^3T_1$ level lies the lowest. Taking into account

16. B. N. Figgis, Nature, Lond. 182, 1568 (1958).
17. B. N. Figgis, Introduction to Ligand fields. Interscience, New York (1966).

the effect of spin-orbit coupling and magnetic field. Figgis has calculated the magnetic moment as a function of kT/λ where λ is the spin-orbit coupling constant. His results indicate that in both cases the magnetic moment increases quite sharply with temperature in the range 80–300°K. Our data on the magnetic susceptibility of dithiooxamidonickel eliminate the possibility of the existence of tetrahedral nickel(II) species in this compound. Apparently all complexes which have nickel co-ordinated to four sulphur atoms are square planar; it seems unlikely that even if here the nickel is co-ordinated to two sulphur atoms and two nitrogen atoms that the nickel would take up the much less common tetrahedral configuration.

A pure octahedral configuration would normally give a moment closely corresponding to two unpaired electrons. Since the magnetic susceptibility follows a Curie Law fairly closely, it is unlikely there is appreciable antiferromagnetic exchange. The low value of μ_{eff} cannot arise from this possibility. If we assume at present that the material is polymeric then we propose the following explanation for the observed paramagnetism. The polymer may be regarded as containing mainly planar units with a proportion of octahedral sites. These latter sites may arise from the interaction between the nickel atom and sulphur or nitrogen atoms in adjacent planes or co-ordination of water molecules. However, dehydrating the compound does not remove the paramagnetism. The percentage of octahedral sites has been calculated from the observed magnetic data by taking μ (octahedral) = 3·0 B. M. and μ (planar) = 0. These values are shown in Table 3. It is seen that the percentage of octahedral sites increases with increasing nickel content. These sites would presumably be randomly arranged.

Table 3. Percentage octahedral sites in various nickel complexes

Substance	Ni (%)	μ_{obs} (Room temp.)	Octahedral sites (%)
Dithiooxamidonickel(II) A	29·2	1·13	14
B	30·8	1·45	23
C	33·7	1·47	24
D	29·1	1·31	19
N,N'-dimethyl-dithiooxamidonickel(II) A	29·1	2·05	47
B	28·96	2·30	59
C	27·84	2·32	60
N,N'-bis(hydroxyethyl)-dithiooxamidonickel(II) A	20·60	1·96	43
B	20·60	2·03	46
C	20·70	2·01	45
N,N'-bis(carboxyethyl)-dithiooxamidonickel(II) A	26·82	2·07	48
B	27·46	2·77	85
C	27·22	2·34	61

Ballhausen and Liehr[18] have explained the paramagnetism of certain square planar complexes of nickel(II) by assuming that, in presence of a fairly strong tetragonal field, $^3A_{2g}$ level can lie close to the ground state $^1A_{1g}$ and when the separation between these levels becomes comparable to kT the $^3A_{2g}$ level can be populated. One would expect that, under such circumstance, the magnetic moment of the complex would be strongly temperature dependent. Our observed data of the magnetic moment of the dithiooxamidonickel(II) cannot be explained on this model.

(II) N,N'-dimethyldithiooxamidonickel(II)

The analytical results for this compound correspond most closely to an anhydrous product except for II A. The analysis does not agree with the polymeric formula suggested by Hurd *et al.* but corresponds very closely to a 1 : 1 product. These samples were prepared by neutralisation with ammonia, whereas Hurd used either sodium hydroxide or sodium acetate.
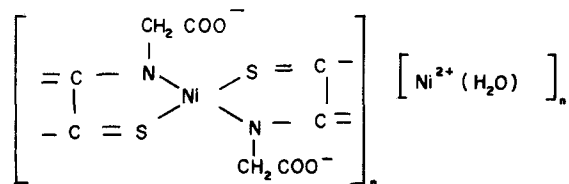
Preparation A has a magnetic moment of 2·1 B.M. while the other three are close to 2·3 B.M. The susceptibility of the sample follows Curie-Weiss Law with a very small value of θ. The moment is slightly lower than the room temperature value found by Hurd. We propose that the paramagnetism arises as in the dithiooxamide complex, but the proportion of octahedral sites (Table 3) is very much greater. This may be caused by distortions introduced by the CH_3 groups.

(III) N,N'-bis(hydroxyethyl)dithiooxamidonickel(II)

The analysis corresponds most closely to a monohydrate. All three preparations give a magnetic moment of 1·9–2·0 B.M. The susceptibility obeys a Curie-Weiss Law with a θ value of about 25°. From our calculations we estimate that about 45 per cent of the nickel atoms occupy octahedral sites.

(IV) N,N'-bis(carboxymethyl)dithiooxamidonickel(II)

The analysis of this compound indicates that the metal atoms are involved not only in chelate formation but also in salt formation, which may be indicated as follows:

$$\left[\begin{matrix} & & CH_2\,COO^- & & \\ & & | & & \\ =C & - & N \diagdown \diagup S & = C- \\ | & & \diagup Ni \diagdown & | \\ -C & = S & \diagup \diagdown N & - C= \\ & & | & \\ & & CH_2\,COO^- & \end{matrix} \right]_n \left[Ni^{2+}\,(H_2O) \right]_n$$

A number of samples prepared under different conditions show that the composition of the compound is also variable. The colour of the various samples ranged from yellow to brown-red. The analytical data are included in Table 1; the nickel to ligand ratio is close to 2 : 1 in all cases. Various samples gave effective magnetic moments ranging from 2·0 to 2·7 B.M. The magnetic moment is definitely temperature dependent and the plot of $1/\chi'_m$ vs. T has a θ value of about

18. C. J. Ballhausen and A. D. Liehr, *J. Am. chem. Soc.* **81**, 538 (1959).

60°. The origin of this large value is not at present obvious. The nickel ions involved in salt formation in this complex will presumably have an octahedral configuration involving water molecules. Over half the nickel atoms appear to be octahedral.

Attempts have been made to prepare crystalline samples so that speculation about the structure may be resolved by X-ray analysis. So far no samples have been obtained which give a well defined X-ray pattern.

Whilst physical properties such as solubility and variable composition indicate that these compounds are polymeric, the i.r. evidence quoted by Barcelo and by Hurd cannot be taken as conclusive. The work of Spinner[19], Milligan *et al.*[20] and Rao and Venkataraghavan[21] show that the detection of the $C=S$ stretching frequency is very difficult in the presence of NH_2 groups because the bands are all combination bands. A further analysis of the spectra of the dithiooxamide complexes is required before the results may be regarded as conclusive.

19. E. Spinner, *J. org. Chem.* **23**, 2037 (1958).
20. B. Milligan, E. Spinner and J. M. Swan, *J. chem. Soc.* 1919 (1961).
21. C. N. R. Rao and R. Venkataraghavan, *Spectrochim. Acta* **18**, 541 (1962).