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Complexes of Nickel(II) with Mononitroso- and Dinitroso-resorcinols

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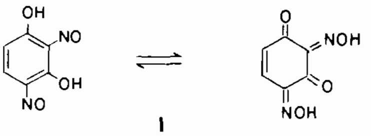
Polymeric complexes of the type Ni(X-dnr)·2L have been prepared, where X-dnrH$_2$ is 2,4-dinitrosoresorcinol, 6-ethyl-2,4-dinitrosoresorcinol, and 5-methyl-2,4-dinitrosoresorcinol and L is water or pyridine. The hydrated complexes have been obtained by nitrosation of resorcinol, 4-ethylresorcinol, and 5-methylresorcinol in the presence of nickel(II) chloride. Nitrosation of 2-methylresorcinol gives Ni(2-Memnr)·4H$_2$O (2-MemnrH = 2-methyl-4-nitrosoresorcinol). In the complexes Ni(X-dnr)·2H$_2$O magnetic susceptibility studies indicate antiferromagnetic interaction through the bridging X-dnr^{2-} ligand.

Introduction

2,4-Dinitrosoresorcinol (I) (dnrH$_2$) exhibits tautomerism and forms complexes with several metals [1–3]. With a divalent metal it could react to form a coordination polymer, containing the catenating dianion dnr^{2-}, which can be represented in valence-bond terms as a resonance hybrid of structures (IIa) and (IIb).



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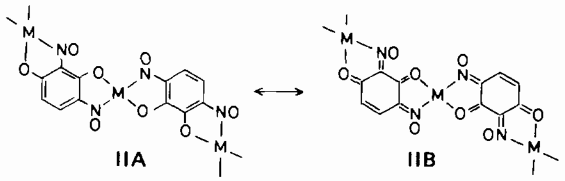

IIA IIB

2,4-Dinitrosoresorcinol could also react with a divalent metal by loss of one hydrogen to give complexes such as M(dnrH)$_2$, containing the monoanion dnrH$^-$. Complexes of 2,4-dinitrosoresorcinol with cobalt, iron, nickel and copper have been reported. Although some of these compounds have found use as dyes and analytical reagents they have not been fully characterised.

In this paper we describe the preparation, characterisation and report on magnetic studies of nickel(II) complexes derived from 2,4-dinitrosoresorcinol, 5-methyl-2,4-dinitrosoresorcinol (5-MednrH$_2$), 6-ethyl-2,4-dinitrosoresorcinol (6-EtdnrH$_2$) and 2-methyl-4-mononitrosoresorcinol (2-MemnrH). The

TABLE I. Analytical and Magnetic Data for Ni(II) Complexes of Nitrosoresorcinols.

Phenol	Product		Yield (%)	Found (%)				Requires (%)				μ_{eff}, B.M. (*ca.* 295 K)
	Formula	No.		C	H	N	Ni	C	H	N	Ni	
Resorcinol	Ni(dnr)·2H$_2$O	1	85	27.9	1.7	10.8	21.4	27.6	1.6	10.7	22.4	2.88
4-Ethylresorcinol	Ni(6-Etdnr)·2H$_2$O	2	95	32.9	3.2	9.4	20.7	33.3	3.5	9.7	20.3	2.94
5-Methylresorcinol	Ni(5-Mednr)·2H$_2$O	3	95	30.2	2.4	10.9	22.8	30.6	2.9	10.2	21.3	2.90
2-Methylresorcinol	Ni(4-MemnrH)$_2$·4H$_2$O	4	48	38.0	2.5	6.4	13.2	38.7	4.6	6.4	13.5	–
	Ni(6-Etdnr)·2py	5	77	52.6	4.0	13.8	14.2	52.7	3.9	13.6	14.3	2.95

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TABLE II. Analytical and Other Data for Nitrosoresorcinols.

Compound	Yield (%)	Found (%)			Requires (%)			M.p. (t/°C)	¹H N.m.r. Spectra	Mass Spectrum P⁺ (m/e)
		C	H	N	C	H	N			
2,4-Dinitrosoresorcinol monohydrate	68	38.4	3.3	15.1	38.7	3.2	15.1	166–7[b] dec.	2.07 2.22 3.46 3.61	168
3-Ethyl-2,4-dinitrosoresorcinol monohydrate	81	44.4	4.4	12.7	44.7	4.6	13.0	150–2 dec.	2.33 8.79 8.90 9.0 7.40–7.75	196
5-Methyl-2,4-dinitrosoresorcinol monohydrate	75	41.8	3.6	13.9	42.0	4.0	14.0	130 dec.	3.60 7.88	182
2-Methyl-4-nitrosoresorcinol	60	54.9	5.8	9.3	54.9	4.6	9.1	146–8 dec.	2.4 2.58 3.57 7.41–7.56 8.21	153

[a] $(CH_3)_2SO$ solvent. [b] Lit., m.p. 168 °C dec. (Ref. 1).

investigation relates to our continuing studies of complexes derived from 2-nitrosophenols [4, 5].

Experimental

Preparation of the Complexes Ni(X-dnr)·2H$_2$O (X = H, 6-Et, and 5-Me) and Ni(2-Memnr)$_2$·4H$_2$O by Nitrosation of Resorcinols

The resorcinol (*ca.* 6 g, 1 mol equiv) in ethanol (100 cm^3) was added to a solution of nickel(II) chloride (1 mol equiv) acetic acid (20 cm^3) and sodium acetate (20 g) in water (120 cm^3). Sodium nitrite (10 g) in water (60 cm^3) was then added in one portion with stirring. The mixture was stirred for one week and then *the product* was filtered off, washed thoroughly by stirring with water (3 X 100 cm^3) and ethanol (3 X 100 cm^3) for several hours and dried at 50 °C/0.1 mm (see Table I for analysis and other data).

Interaction of the Complex Ni(6-Etdnr)·2H$_2$O with Pyridine

The hydrated complex (*ca.* 3 g) was heated in pyridine (100 cm^3) at 100 °C for 1 h. The reaction mixture was filtered hot, the filtrate was evaporated to dryness at 60 °C/0.1 mm, and the resultant residue of *the pyridine adduct* was washed with ethanol and ether and dried at 100 °C/0.1 mm (see Table I for analysis of other data).

Interaction of the Complexes Ni(X-dnr)·2H$_2$O and Ni(2-Memnr)$_2$·4H$_2$O with Aqueous Hydrochloric Acid

Concentrated hydrochloric acid (10 cm^3) was added to a well stirred suspension of the complex (*ca.* 3 g) in water (50 cm^3) and the mixture was stirred for 1 h. *The protonated ligand* was filtered off, washed with dilute hydrochloric acid and then with water and dried at 20 °C/0.1 mm (see Table II for analysis and other data).

Measurements

Thermogravimetric analysis data (Table III), magnetic susceptibility data, and electronic and mass spectra were obtained as described earlier [4,5].

^{1}H n.m.r. spectra were recorded at 60 MHz on a Perkin-Elmer 12B spectrometer using deuterated dimethylsulphoxide as solvent and tetramethylsilane as internal standard.

Results and Discussion

Bottei and McEachern [1] reported that the reaction of nickel acetate with 2,4-dinitrosoresorcinol in aqueous ethanol gave a product which they formu-

TABLE III. Thermogravimetric Analysis Data.

Compound[a]	Wt. of Sample (mg)	T/°C[b]	Weight Loss (mg)		Decomposition Temperature (°C) of Ni(X-dnr)[d]
			Found	Calc[c]	
1	206	165	24	28	235
2	191	155	28	24	260
5	149	180	56	57	260

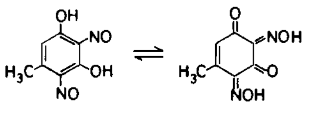
[a]Nos. from Table I. [b]Temperature of loss of water or pyridine. [b,d]Maxima on the rate of weight loss against temperature curve. [c]Calc. for 2 mol equiv of water or pyridine.

TABLE IV. Variable Temperature Magnetic Data for Ni(5-Mednr)·$2H_2O$ and Ni(6-Etdnr)·$2H_2O$.

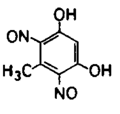
Ni(5-Mednr)·$2H_2O$										
T/K	314.2	297.7	273.1	246.2	216.7	187.2	155.3	128.2	98.8	83.2
$10^6 \chi_A$	3381	3536	3624	3942	4335	4780	5327	6033	7116	7827
μ_{eff}	2.92	2.90	2.82	2.79	274	2.68	2.57	2.49	2.37	2.28
$-\theta$/K	92									
Ni(6-Etdnr)·$2H_2O$										
T/K	297.2	273.1	246.2	216.7	187.2	155.3	128.2	98.8	91.2	
$10^6 \chi_A$	3655	3906	4236	4623	5164	5713	6474	7555	7193	
μ_{eff}	2.94	2.92	2.89	2.83	2.78	2.67	2.58	2.45	2.39	
$-\theta$/K	86									

lated as the polymeric complex Ni(dnr)·H_2O. In contrast, Hunter and Webb [2] reported that interaction of a nickel salt with 2,3-dinitrosoresorcinol in methanol followed by precipitation with diethyl ether, gave a complex which they formulated as Ni(dnrH)$_2$·$4H_2O$. We have obtained a polymeric complex of formula Ni(dnr)·$2H_2O$ by nitrosation of resorcinol in the presence of nickel chloride. The analogous complexes Ni(5-Mednr)·$2H_2O$ and Ni(6-Etdnr)·$2H_2O$ have been obtained similarly by nitrosation of 5-methylresorcinol and 4-ethyl-resorcinol respectively. In contrast, nitrosation of 2-methylresorcinol in the presence of nickel chloride led to mononitrosation and formation of the complex Ni(2-Memnr)$_2$·$4H_2O$. Attempts to dinitrosate 2-methylresorcinol using acetic acid and sodium nitrite in aqueous media were unsuccessful. Nitrosation using amyl nitrite in ethanolic sodium hydroxide also gave the mononitroso derivative.

The formulation of the complexes was established by elemental analysis and i.r. spectroscopy. In each case the position of nitrosation was determined by acidifying the complex and characterizing the liberated protonated ligand (some properties of the protonated ligands are given in Table II). Thus the complex obtained by nitrosation of 2-methylresorcinol on treatment with aqueous hydrochloric acid gave 2-methyl-4-nitrosoresorcinol as indicated by elemental analysis, mass spectrometry, and by the proton n.m.r. spectrum which showed a quartet due to two non-equivalent ring protons in positions 5 and 6. The complex obtained from 4-ethylresorcinol on treatment with aqueous hydrochloric acid gave 6-ethyl-2,4-dinitrosoresorcinol monohydrate which was formulated on the basis of elemental analysis and of the mass spectrum which indicated a molecular weight of 196 for the anhydrous compound. The alternative formulation of the hydrated ligand as 6-ethyl-2,5-dinitrosoresorcinol is precluded because a requirement for the formation of a coordination polymer by chelation is that the nitroso and hydroxy groups are in ortho positions. In the case of the complex derived from 5-methylresorcinol analytical, n.m.r. and mass spectral data indicate that the protonated ligand is either 5-methyl-2,4-dinitrosoresorcinol (III) or 5-methyl-4,6-dinitrosoresorcinol (IV).



III



IV

The complexes Ni(X-dnr)·$2H_2O$ (X = H, 6-Et, and 5-Me) were insoluble in common organic solvents but dissolved in hot pyridine to give pyridine adducts as indicated by the isolation and characterisation of such an adduct when X = 6-Et. Thermogravimetric analysis (Table III) on all the hydrates and the pyridine adduct Ni(6-Etdnr)•2py showed that water or pyridine was lost between 150–180 °C to give Ni(X-dnr) which decomposed between 235–260 °C.

Magnetic susceptibilities for the complexes Ni(X-dnr)•$2H_2O$ and Ni(6-Etdnr)•2py were measured and the calculated magnetic moments are given in Table I. The room temperature moments are close to the low limit of the range (3.0–3.4 B.M.) expected for magnetically dilute nickel(II) in an approximately octahedral field. However, the decreasing magnetic moment with temperature (Table IV) and the negative Weiss constants (*ca.* –90 K) observed for two of the complexes subjected to measurements at variable temperature support antiferromagnetic interaction through the bridging X-dnr^{2-} ligand.

Acknowledgements

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