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Inorganica Chimica Acta 223 (1994) 71–75

Inorganica Chimica Acta

Metal complexes of some 2-nitrosoanilides

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Received by Editor 26 July 1993; received by Publisher 14 April 1994

Abstract

In the presence of a base 2-nitrosoanilines react with metal salts to give metal complexes. A total of nineteen compounds is described derived from salts of copper(II), nickel(II), palladium(II), mercury(II) and iron(III) with two primary anilines (2-nitroso-4-methylaniline and 2-nitroso-4,6-dimethylaniline) and two secondary anilines (2-nitroso-4,*N*-dimethylaniline and 2-nitroso-4-methyl-*N*-ethylaniline). In the absence of a base the binuclear complex di-μ-chlorobis(2-nitroso-4-methyl-*N*-ethylphenylamidopalladium(II)) is formed. IR, mass spectroscopic, ESR and magnetic susceptibility measurements show all the metals to be N-bonded by the nitroso group. The nickel(II), palladium(II) and iron(III) compounds are low spin complexes. The nickel(II) complexes are monomeric and show only a small tendency to act as Lewis acids. The values of K are reported for the formation of two complexes NiL_2·pyridine where the ligands, L, are the anions, 2-nitroso-4-methylphenylamido and 2-nitroso-4-methyl-*N*-ethylphenylamido. Comparisons are made between these compounds and the analogous complexes of 2-nitrosophenols.

Keywords: Metal complexes; Nitrosoanilide complexes

1. Introduction

The metal complexes of 2-nitrosoanilines have not previously been described. This is in marked contrast to the complexes of the 2-nitrosophenols which have been known since 1902 [1] and have been well investigated [2,3][1]. This paper describes the preparation of several 2-nitrosoaniline complexes and compares them with 2-nitrosophenol complexes.

2. Experimental

The four 2-nitrosoanilines were prepared by the literature [4,5] methods.

2.1. Preparation of the metal complexes (see Table 1).

A methanolic solution of the 2-nitrosoaniline containing an equimolar amount of sodium hydroxide was added to the stoichiometric quantity of the metal salt in methanol. The metal salts were anhydrous iron(III) chloride, nickel(II) chloride hexahydrate, dichlorobisbenzonitrilepalladium(II), copper(II) perchlorate hexahydrate or copper(II) acetate monohydrate and mercury(II) acetate. The reactants were stirred together for 4 h at room temperature and the precipitated product filtered off. The product was either washed with solvent W, or recrystallised from solvent R, or dissolved in chloroform, the solution filtered and concentrated and the complex precipitated by the addition of solvent P (see Table 1).

2.2. Preparation of di-μ-chlorobis(2-nitroso-4-methyl-N-ethylphenylamidopalladium(II)

A solution of 2-nitroso-4-methyl-*N*-ethylaniline (2 mol) in chloroform was added to a stirred suspension of palladium(II) chloride (1 mol) in chloroform. After stirring for 12 h at room temperature the solution was filtered, evaporated to dryness and the residue recrystallised from toluene giving black needless of the product.

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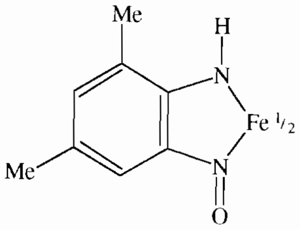
[1] The work of Charalambous and co-workers [2] includes examples of crystal structures, solution electronic spectra, mass spectra, association in solution, formation of adducts, magnetic properties and reactions with donor molecules.

Elsevier Science S.A.
SSDI 0020-1693(94)04000-L

Table 1
Preparation of the metal complexes

Complex[a]	Method[b]	Yield (%)	Found (calc.) (%)				$\mu_{eff}/\mu B$, 298 K
			C	H	N	M	
$[PdLCl]_2$ (4Me,NEt)	R, toluene	81	36.0 (35.4)	3.4 (3.6)	9.4 (9.2)	36.0 (35.0)	Cl 11.7% (Cl 11.6%)
CuL_2 (4Me)	P,lt petrol b.p. 40–60°	84	50.1 (50.4)	4.1 (4.2)	16.5 (16.8)		1.9
CuL_2 (4,6diMe)	P,Et_2O	78	53.1 (53.1)	5.1 (5.0)	15.2 (15.5)		1.9
CuL_2 (4,NdiMe)	W,MeOH	79	53.1 (53.1)	5.1 (5.0)	15.4 (15.5)		0.9
HgL_2 (4,6diMe)	R,EtOH	82	38.5 (38.5)	3.6 (3.6)	10.9 (11.2)		
HgL_2 (4Me,NMe)	R,EtOH	91	38.5 (38.5)	3.6 (3.6)	11.3 (11.2)		
	Mössbauer parameters						
	IS (mm s^{-1})	QS	ω				
FeL_3 (4,6diMe)	0.1	1.13	0.34(3), 0.35(3)				
FeL_3 (4,NdiMe)	0.1	1.47	0.4 0.37				

[a] FeL_3(4,6-diMe) is tris(2-nitroso-4,6-dimethylphenylamido)iron(III)



[b] The solvents used for washing W, recrystallisation R, or precipitation P.

[c] Sticky products requiring trituration with diethyl ether.

2.3. Preparation of N-deuterated nickel(II) and palladium(II) complexes

A few drops of dry triethylamine were added to the N-deuterated 2-nitroso-*N*-alkylaniline in CD_3OD and the solution added to the tetradeuteromethanolic solution of either anhydrous nickel(II) chloride or dichlorobisbenzonitrilepalladium(II). The solutions were stirred for 4 h at room temperature and the resulting black solids filtered off, washed with dry diethyl ether and dried in vacuo.

All the reactions were carried out using about 5 mmol of the aniline for each preparation. All the products were black.

Yields, methods of purification, microanalyses and magnetic data are listed in Table 1.

2.4. Analytical and physical data

The elemental analyses were carried out in the microanalytical laboratory of the Chemistry Department at UMIST.

IR spectra in the 4000–400 cm^{-1} range were measured on mulls between KBr plates using Perkin-Elmer 735 and 783 spectrophotometers. Far-IR spectra in the range 400–50 cm^{-1} were recorded on a Beckman IR-720M spectrophotometer. Absorption electronic spectra were recorded on a Beckman model 25 spectrophotometer incorporating a variable temperature unit. Proton NMR data were recorded on Bruker WP80 and Varian XL 300 MHz Fourier transform spectrophotometers in $CDCl_3$ using Me_4Si as the internal reference. Mass spectra were determined using a MG45 Kratos spectrometer by direct insertion into the ionisation chamber at 250 °C using an ionisation potential of 70 eV. Magnetic moments were measured by the Gouy method using $HgCo(CNS)_4$ as the calibrant. Electron spin resonance spectra were recorded on a Varian Eg spectrometer at room temperature and −170 °C.

3. Results and discussion

Table 2 presents the IR spectral data of all the compounds prepared. Their similarity to each other suggests that the structures of the metal complexes are similar too. Deuteration of the N–H group in the primary amines and their metal complexes enables δ(N–H) and ν(CN), both in the 1200–1380 cm^{-1} range, to be distinguished.

Comparison between the data in Table 2 and the IR data for the free anilines [6] agrees with the changes in bond lengths detected by single crystal X-ray diffraction structure determination [7,8]. On coordination to palladium(II) *d*(N–O) increases slightly and ν(NO) decreases; *d*(C–NO) decreases and ν(CN) increases. Thus the bonding in the ligand suffers a small change on coordination from the nitrosoaniline structure towards the tautomeric benzoquinoneimine form.

The IR spectra of the compounds formulated $[PdLCl]_2$ show two absorptions at 286 and 345 cm^{-1} not present in either the ligand or PdL_2. These are characteristic of a μ-dichloro bridged binuclear compound [9].

3.1. ^1H NMR spectra

Because of low solubility the NMR spectra of only one nickel and five palladium complexes were analysed and compared with those of the parent ligands. The results are presented in Table 3. The spectrum of $[PdLCl]_2$ showed some doubling of the spectrum suggesting that *cis* and *trans* isomers may exist in similar concentrations in solution.

On complexation all the proton resonances move downfield with the 3-H resonance affected more than any other, moving from δ 8.3 in the ligand to δ 6.7 in the complex. This can be interpreted as some movement of electron density from the amine nitrogen atom to the nitroso nitrogen atom, i.e. a structure change from the nitroso tautomer towards the oxime form.

3.2. Lewis acidity

The electronic spectra of chloroform solutions of the four nickel(II) complexes indicate adduct formation when small amounts of pyridine are added. In each case there are at least three isosbestic points in the range 300–800 nm. Therefore the only species present

Table 2
Characteristic IR absorptions of metal complexes of 2-nitrosoanilines

Compound	ν(N–H) (cm^{-1})	ν(N–O) (cm^{-1})	ν(CN) (cm^{-1})	δ(N–H) (cm^{-1})
CuL_2(4,6diMe)	3375(m)	1530(m)	1330(s)	1188(m)
NiL_2	3365(m)	1520(s)	1342(s)	1185(m)
NiL_2[a]	(2380(m))[a]	1518(m)	1322(s)	
PdL_2	3370(m)	1523(s)	1340(s)	1200(m)
PdL_2[b]	(2495, 2513(m))[a]	1517, 1538(m)	1328(s)	
HgL_2	3180(s,br)	1517, 1545(m)	1305(m)	
FeL_3	3250(m,br)	1503(m)	1310(s)	
CuL_2(4Me)	3290(m,br)	1540(s)	1335(s)	1208(m)
NiL_2	3307(s)	1531, 1520(m)	1360(s)	1227(s)
NiL_2[a]	(2425(m))[a]	1525, 1513(m)	1350(s)	
PdL_2	3290(s)	1536, 1520(m)	1360(s)	1230(s)
PdL_2[a]	(2430(s))[a]	1520, 1510(m)	1350(s)	
FeL_3	3130(m,br)	1505(s)	1305(m)	
NiL_2(4Me,NMe)		1534(s)	1355(s)	
PdL_2		1538(m), 1522(w)	1355(s)	
HgL_2		1524(m), 1515(w)	1302(s)	
FeL_3		1510(m)	1310(s)	
CuL_2(4Me,NEt)		1550(s)	1315(s)	
NiL_2		1528(m), 1512(w)	1350(s)	
PdL_2[b]		1535(m), 1515(w)	1353(s)	
FeL_3		1510(m)	1315(m)	

s = strong, m = medium, w = weak, br = broad.

[a] The N-deuterated compound and its ν(N–D) absorption.

[b] ν(Pd–Cl) for this compound, 286 and 345 cm^{-1}.

Table 3
^{1}H NMR data for some 2-nitrosoanilines and complexes

Compound	δ Values (ppm vs. TMS)					
	3-H	5-H	6-H/CH_3	4-CH_3	N-H	N-C_2H_5
HL 4,6-diMe	8.18(s)	7.13(s)	2.15(s)	2.08(s)	7.35(s,br)	
NiL_2	6.43(s)	6.35(s)	1.78(s)	1.9(s)		
PdL_2	6.56(s)	6.56(s)	1.95(s)	7.38(s,br)		
HL 4Me,NEt	8.4(s)	7.28(d)	6.79(d)	2.40(s)		3.31(m), CH_2; 1.31(c), CH_3
NiL_2	6.69(s)	6.63(s)	6.63(s)	1.92(s)		3.56(q), CH_2; 1.29(t), CH_3
PdL_2	6.76(t)	6.71(d)	6.71(d)	1.95(d)		3.87(q), CH_2; 1.13(t), CH_3
$[PdLCl]_2$[a]	6.94(s) 6.63(s)	6.66(d)	6.8(d)	2.05(d)		1.35(q), CH_2; 3.82(t), CH_3 1.30(q), CH_2; 3.55(t), CH_3

[a] No attempt has been made to associate these resonances with either isomer.

are NiL_2 and NiL_2 pyridine. Two equilibrium constants were determined, using the change in absorption at 490 nm in each case: K_1 (293 K) for $NiL_2(4,Me)\cdot pyridine = 2.7 \pm 0.4$; K_1 (293 K) for $NiL_2(4Me,NEt)$ pyridine $= 23 \pm 2$. With these small values of K_1 it is not surprising that no pyridine adducts could be isolated. This contrasts with the corresponding 2-nitrosophenol complexes which do form isolable dipyridine adducts [10]. Similarly the spectra of the title compounds show little sensitivity to donor solvents such as ethanol and dimethylformamide, while the nitrosophenol complexes do [11,12].

None of the nickel(II) complexes in chloroform solution showed any temperature sensitivity over the temperature range 5–50 °C. This again contrasts with solutions of the nickel(II) nitrosophenol complexes whose dimers dissociate on heating [3,11]. Mass spectral data reinforce the difference. All the nickel complexes described here give molecular ions containing nickel atoms (only $NiL_2(4,6diMe)_2$ gives the parent ion), but none give binuclear species as some nitrosophenol complexes do [13–15].

3.3. Magnetic properties

The nickel(II), palladium(II) and iron(III) compounds are all low spin complexes, see Table 1. The nickel and palladium complexes are square planar [8] and diamagnetic, the iron(III) complex is a low spin octahedral compound as confirmed by the Mössbauer parameters. The copper(II) complexes of the primary amines have one unpaired electron each and the coordination by four nitrogen atoms is confirmed by electron spin resonance data (Table 4). Both complexes show the four main resonances due to the copper hyperfine structure (I = 3/2). The spectrum of $CuL_2(4,6\text{-}diMe)$ shows the superhyperfine structure of nine lines or shoulders expected for complexation by four nitrogen atoms. The g values and hyperfine structure constants are similar to those found for bis(dimethylglyoximato)copper(II) [16] (Table 4). The copper ion in the secondary amine complex $CuL_2(4,NdiMe)$ is EPR silent, has a low effective magnetic moment, $\mu_{eff} = 0.9$ BM, and is the only copper(II) complex to give a well-defined NMR spectrum. This points to the possibility of Cu–Cu interaction in this complex both in the solid and in solution. An X-ray diffraction crystal structure determination would be useful.

Table 4
EPR resonances for some copper(II) complexes in chloroform solution at room temperature

Compound	g_0	$g_\parallel$	$g_\perp$	$A_\parallel \times 10^4$ (cm^{-1})
$CuL_2(4,6diMe)$	2.032	2.095	2.001	135
$CuL_2(4\text{-}Me)$	2.036	2.098	2.005	133
$Cu(DMG)_2$[a]	2.08	2.15	2.05	144

[a] $Cu(DMG)_2$ is bis(dimethylglyoximato)copper(II) [16].

Finally it is interesting to compare 2-nitrosoanilines and 2-nitrosophenols as ligands. The former act as 2 × N donors and change their structure very little on complexation, that change being towards the imino-oxime form. The latter act as N,O donors and change structure markedly from the 1,2-benzoquinone-2-oxime towards the 2-nitrosophenolate structure [17]. The former are strong field ligands whose nickel(II) complexes are diamagnetic while the latter give the corresponding paramagnetic complexes. The former yield nickel(II) complexes which are weaker Lewis acids and monomeric, the latter form nickel(II) complexes which are dimeric and readily form solvent adducts.

4. Supplementary material

Mass spectra of the parent anilines and of some nickel(II), copper(II) and palladium(II) complexes, and electronic spectra of the complexes in chloroform are available from the author on request.

Acknowledgement

I.M. El-Nahhal acknowledges generous financial support from the University of Qatar.

References

[1] A. Bayer and E. Knorr, *Berichte, 35* (1902) 3034.
[2] R.G. Buckley, J. Charalambous, M.J. Kensett, M. McPartlin, D. Mukerjee, E.G. Brain and M.J. Jenkins, *J. Chem. Soc., Perkin Trans., 1* (1983) 693.
[3] I.M. El Nahhal, G.S. Heaton and A.M. Jelan, *Inorg. Chim. Acta, 197* (1992) 193.
[4] E.Yu. Belyaev, L.H. Gornostaev and S.V. Petrova, *J. Org. Chem. USSR, 11* (1975) 1947.
[5] E.Yu. Belyaev and G.V. Petrova, *J. Org. Chem. USSR, 13* (1977) 1121.
[6] I.M. El Nahhal and G.S. Heaton, *J. Chem. Res. M,* (1989) 2357.
[7] R.G. Pritchard, G.S. Heaton and I.M. El Nahhal, *Acta Crystallogr., Sect. C, 45* (1989) 829.
[8] R.G. Pritchard, G.S. Heaton and I.M. El Nahhal, *Acta Crystallogr., Sect. C, 45* (1989) 815.
[9] D.M. Adams and P.J. Chandler, *Chem. Commun.,* (1966) 69.
[10] J. Charalambous, M.J. Frazer and F.B. Taylor, *J. Chem. Soc. A,* (1971) 602.
[11] H. El Khadem and W.M. Orabi, *Z. Anorg. Allg. Chem., 365* (1969) 315.
[12] C.B. Castellani, G. Gatti and R. Millini, *Inorg. Chem., 23* (1984) 4004.
[13] J. Charalambous, M.J. Kensett and J.M. Jenkins, *Inorg. Chim. Acta, 16* (1976) 213.
[14] J. Charalambous, M.J. Frazer and F.B. Taylor, *J. Chem. Soc. A* (1969) 2787.
[15] J. Charalambous, P. Maple, N.A. Nassef and F.B. Taylor, *Inorg. Chim. Acta, 26* (1978) 107.
[16] A.K. Weirsema and J.J. Windle, *J. Phys. Chem., 68* (1964) 2316.
[17] M. McPartin, *Inorg. Nucl. Chem. Lett., 9* (1973)1207.