Inorganica Chimica Acta, 33 (1979) 265–268
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

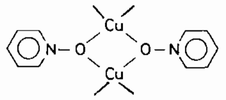
Copper(II) Chloride Adducts with Nicotinic and Isonicotinic Acid N-Oxides

L. S. GELFAND, L. L. PYTLEWSKI
Department of Chemistry, Drexel University, Philadelphia, Pa. 19104, U.S.A.
C. M. MIKULSKI
Department of Chemistry & Physics, Beaver College, Glenside, Pa. 19038, U.S.A.
A. N. SPECA
USI Chemicals Co., Research Division, Cincinnati, Ohio 45237, U.S.A.
N. M. KARAYANNIS
Amoco Chemicals Corporation, Naperville, Ill. 60540, U.S.A.
Received September 12, 1978

CuL_nCl_2 complexes are formed by interaction of nicotinic ($n = 4$) or isonicotinic ($n = 1$) acid N-oxide and $CuCl_2$ solutions in ethanol–triethylorthoformate. The 1:4 $CuCl_2$ adduct with nicotinic acid N-oxide seems to be a dimer of the $[L_3ClCuL_2CuClL_3]Cl_2$ type, with both terminal and bridging, exclusively N–O oxygen-bonded ligand groups. This compound exhibits a subnormal ambient temperature magnetic moment (1.20 μB) and temperature-dependent paramagnetic behavior. The 1:1 $CuCl_2$ adduct with isonicotinic acid N-oxide is apparently polymeric ($[CuLCl_2]_x$), with the ligand functioning as tridentate, bridging, coordinating through all three (N–O and COO) of its oxygens. This formulation is supported by the magnetic evidence, i.e., *normal ambient temperature μ_{eff} of 2.06 μB, and measurable antiferromagnetic exchange at lower temperatures.*

Introduction

Nicotinate and isonicotinate N-oxide (N-nicO and N-inicO, respectively) complexes with 3d metal ions have been synthesized and characterized by these laboratories [1–3]. More recently, work aimed at the syntheses of 3d metal salt (perchlorate [4], chloride or acetate) adducts with the corresponding neutral ligands (nicotinic (N-nicOH) and isonicotinic (N-inicOH) acid N-oxides) was undertaken. During these studies, two rather unusual adducts of $CuCl_2$ with these ligands were isolated. Cu^{2+} chloride or bromide usually form 1:1 and 1:2 adducts with aromatic amine N-oxides [5–7]. Most of the 1:1 and certain 1:2 adducts of these types are N-oxide-bridged dimers (I) and exhibit subnormal magnetic behavior; spin-spin coupling in these compounds occurs by a superexchange mechanism, operating via the orbitals of the bridging oxygen atoms [5–7]. Among the numerous dimeric 1:1 complexes of type (I) reported, Muto *et al.* have isolated the following compounds, involving ligands of interest to the present study: $[CuCl_2(N\text{-}nicOH)]_2$; $[CuX_2(L)]_2$ (X = Cl,Br; L = N-nicOC$_2$H$_5$, N-inicOC$_2$H$_5$). All these complexes are characterized by very low ambient temperature (298 K) magnetic moments, ranging between 0.28–0.54 μB, and were precipitated by briefly heating a mixture of stoichiometric quantities of the anhydrous Cu^{2+} halide and the ligand in ethanol [7].



(I)

Under our synthetic conditions, 3.2 mmol of the ligand (N-nicOH or N-inicOH) were mixed with 30 ml of a 3:2(v/v) ethanol–triethyl orthoformate (teof) mixture and heated to 60 °C for 2–3 hr. 1 mmol anhydrous $CuCl_2$ was treated in the same manner with 10 ml of ethanol–teof mixture. Then, the warm mixture of the ligand with the solvent mixture (containing some undissolved amount of ligand) was filtered through a sintered-glass funnel and the filtrate was immediately mixed with the $CuCl_2$ solution. The resulting mixture was refluxed for 1½ hr, and the precipitate formed at the end of this treatment was separated by filtration, washed with warm ethanol–teof, and stored in an evacuated desiccator over anhydrous $CaSO_4$. The new yellow-green complexes have the following stoichiometries: $CuCl_2(N\text{-}nicOH)_4$: Analysis, found (calc.)%: C 41.39 (41.72); H 3.02(2.92); N 7.80(8.11); Cl 10.55(10.26); Cu 9.49(9.20); $CuCl_2(N\text{-}inicOH)$: Analysis: C 26.68(26.34); H 1.82(1.84); N 5.25(5.12); Cl 25.59(25.92); Cu 23.70(23.23). The N-nicOH complex is rather sparingly soluble in organic

TABLE I. Spectral and Magnetic Data for $CuCl_2$ Adducts with N-nicOH and N-inicOH.

	$CuCl_2$(N-nicOH)$_4$	$CuCl_2$(N-inicOH)
Solid-state (Nujol mull)		
electronic spectrum, nm^a	202vvs, 214vvs, sh, 222vvs, 270vs, b, 282vs, sh, 307vs, sh, 333vs, b, 415s, b, 675m, sh, 720m, sh, 760m, 815mw, sh	222vs, sh, 277vvs, 296vvs, vb, 314vvs, sh, 347vvs, vb, 880s, vvb
Infrared Data, cm^{-1}		
$\nu_{C=O}$^{b}	1726s	1713vw, 1694vw, 1590vvs
ν_{C-O}^{b}	1448m, 1391m	1397vvs, b, 1370s
ν_{N-O}^{b}	1201m, sh, 1194m	1210vs, 1204vs
$\nu_{Cu-O(N-O)}$	382w, b, 330m, 289m	440s, 381m
ν_{Cu-O}(C=O or C–O)	–	362m, 320m
ν_{Cu-Cl}	259s	282m, 237m

Magnetic Data

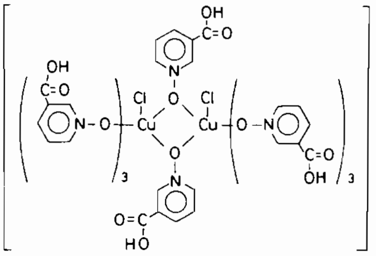
T, K	$10^6\chi_M^{cor}$, cgsu	μ_{eff}, μB	T, K	$10^6\chi_M^{cor}$, cgsu	μ_{eff}, μB
299.9	600	1.20	296.8	1780	2.06
243.9	627	1.11	278.5	1888	2.06
206.7	678	1.06	259.6	2004	2.05
170.7	707	0.99	241.8	2143	2.04
117.9	870	0.91	222.8	2293	2.03
100.4	963	0.88	204.7	2491	2.03
81.7	1096	0.85	187.2	2693	2.02
			169.3	2941	2.00
			151.5	3236	1.99
			133.9	3625	1.98
			116.9	4092	1.96
			99.4	4714	1.94
			81.2	5493	1.90
			79.7	5477	1.88

Abbreviations: s, strong; m, medium; w, weak; b, broad; v, very; sh, shoulder.
[a] Electronic spectra of the ligands, nm: Nujol mulls: N-nicOH: 204vs, 217vs, 269vvs, 290vvs, vb, 310vs, sh; N-inicOH: 218vs, sh, 261vvs, sh, 284vvs, b, 311vs, sh (3); aqueous solutions: N-nicOH: 220, 260, 306sh; N-inicOH: 216, 280 (22). [b] Ligand ir bands, cm^{-1}: N-nicOH: $\nu_{C=O}$ 1710vs; ν_{C-O} 1436vs; ν_{N-O} 1270vs; N-inicOH: $\nu_{C=O}$ 1720vs, 1708vs; ν_{C-O} 1439vs; ν_{N-O} 1290vs (8).

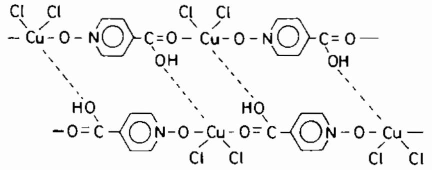
media, including nitromethane (molar conductivity of a 10^{-3} *M* solution of the complex in this solvent at 25 °C is $\Lambda_M = 76\ \Omega^{-1}\ cm^2\ mol^{-1}$), while the new N-inicOH complex is insoluble in all common organic solvents.

Pertinent infrared and electronic spectral data, as well as magnetic susceptibility measurements at 80–300 °K (obtained courtesy of Dr. A. B. P. Lever at York University in Toronto) are shown in Table I. The ir evidence is clearly indicative of coordination of the N-oxide ligands though the N–O oxygen in both complexes (shifts of ν_{N-O} to lower wavenumbers, relative to the location of this mode in the uncomplexed pyridine carboxylic acid N-oxides [8]) [9]. The N-nicOH complex seems to involve ligand groups coordinating only though the N–O oxygen, with the C=O and C–O(H) oxygens remaining uncoordinated (positive $\nu_{C=O}$ frequency shift and a split ν_{C-O} absorption with maxima at both higher and lower wavenumbers relative to ν_{C-O} in free N-nicOH). In the case of the N-inicOH complex, in addition to coordination through the N–O oxygen, the ligand appears to be also coordinated through the C=O [10–13] and possibly the C–O(H) oxygen, as suggested by the negative $\nu_{C=O}$ and ν_{C-O} frequency shifts. Tentative metal–ligand band assignments in the lower frequency ir region are compatible with coordination numbers six for the N-nicOH complex [1–3, 14–16] and five for the new N-inicOH complex [1–3, 17, 18]. Significantly large splittings of the $\nu_{Cu-O(N-O)}$ bands of $CuCl_2$(N-nicOH)$_4$ are indicative of the presence of both terminal and bridging N–O oxygen-bonded N-nicOH ligands [19]. The d–d transition spectrum of $CuCl_2$(N-nicOH)$_4$ is characterized by a split, broad absorption, with the most intense bands located at 675–760 nm; the splitting of the $^2E_g \rightarrow {}^2T_{2g}$ transition presumably arises from low symmetry components in the ligand field [1, 20]; the complex is, thus, hexacoordinated, but not purely octahedral (approximate Dq of 1393 cm^{-1}). As far as the d–d transition spectrum of $CuCl_2$ (N-inicOH) is concerned, the broad band with its maximum at 880 nm is very similar to that observed in most dimeric 1:1 complexes of $CuCl_2$ with aromatic amine N-oxides [7]; the crystal structure of complexes of this type has been shown to involve coordination number five, arising by the presence of "long" Cu–Cl bonds between adjacent dimeric units of type (I) [21]. The two new Cu^{2+} complexes exhibit similar UV spectra to those observed for the $CuL_2 \cdot xH_2O$ compounds (L = N-nicO^- or N-inicO^-) [1–3], *i.e.*, shifts and splittings of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the ligands (3, 22), and charge-transfer bands at 333–347 nm [23]. As was also the case with the N-nicO^- or N-inicO^- 3d metal complexes [1–3], the maximum of the charge transfer band of the new N-nicOH complex appears at significantly higher energy than the corresponding maximum in the N-inicOH complex. The view that this is due to the substantially weaker electron-withdrawing effect of the *meta-* relative to the *para-*COOH substituent (σ_{pyNO} constants: 3-COOH 0.335; 4-COOH 0.608 [24]) was previously advanced [1, 3].

The ambient temperature magnetic moment of $CuCl_2(N\text{-}nicOH)_4$ is clearly subnormal (1.20 μB) and temperature-dependent, showing a μ_{eff} decrease of 0.35 μB at 300–80 K. The magnetic evidence is, thus, in favor of a structure involving bridging of type (I) for this complex [5–7, 25]. The hexacoordinated structure (II), which includes both terminal and bridging N–O oxygen-bonded N-nicOH ligands, as well as both coordinated and ionic chloro groups (since the Λ_M value for the complex in nitromethane, *i.e.*, 76 Ω^{-1} cm^2 mol^{-1}, is typical for a 1:1 or 2:2 electrolyte [26]), is compatible with the overall evidence. It should be noted that the isolation of a 1:4 complex of $CuCl_2$ with an aromatic amine N-oxide is unprecedented. On the other hand, the 1:1 complex of $CuCl_2$ with N-inicOH exhibits a normal ambient temperature magnetic moment (2.06 μB). The decrease of μ_{eff} with decreasing temperature for this compound is considerably smaller than that observed for the N-nicOH complex at 300–80 K; thus, at 300–135 K the μ_{eff} of $CuCl_2$-(N-inicOH) decreases by *ca.* 0.01 μB for each temperature decrease of about 20°, while at 135–80 K it shows a somewhat sharper decrease. These features are considered as favoring a polymeric structure involving  $-Cu-O-NC_5H_4\overset{OH}{C}=O-Cu$ bridges rather than a structure of type (I). In fact, Cu^{2+} compounds, characterized by the presence of bidentate bridging aromatic amine or amine N-oxide ligands, do not necessarily exhibit subnormal room temperature magnetic moments, but show measurable antiferromagnetic exchange at lower temperatures (occurring by an extended π pathway mechanism, involving overlap of the π and π^* orbitals of the heterocyclic ligand with the symmetric and antisymmetric combinations of the copper orbitals) [25, 27–29]. Hence, the overall evidence is in favor of a structure like (III) for the new N-inicOH complex, involving two linear polymeric units with bidentate bridging (N–O and C=O oxygen-bonded) ligand groups, and coordination number five arising by coordination between C–O(H) oxygens and Cu^{2+} ions of neighboring linear chains. It is worth mentioning that the formation of a 1:1 $CuCl_2$–aromatic amine N-oxide polymeric adduct, comprising tridentate bridging ligand groups rather than the common dimeric structure (I) is quite unusual and apparently due to the pronounced tendency of isonicotinic acid and its derivatives to function as bi- or tri-dentate bridging ligands [3, 30].



(II)



(III)

References

1 A. N. Speca, L. S. Gelfand, L. L. Pytlewski, C. Owens and N. M. Karayannis, *Inorg. Chem.*, *15*, 1493 (1976); *J. Inorg. Nucl. Chem.*, *39*, 537 (1977).

2 L. S. Gelfand, L. L. Pytlewski, D. L. Cosgrove, C. M. Mikulski, A. N. Speca and N. M. Karayannis, *Inorg. Chim. Acta*, 27, *L97 (1978)*.

3 *Idem, ibid.*, *32*, 59 (1979).

4 A. N. Speca, L. S. Gelfand, F. J. Iaconianni, L. L. Pytlewski, C. M. Mikulski and N. M. Karayannis, *Proceedings, XIX ICCC, Prague, Czechoslovakia, September 4–8* (1978) Vol. II, 116a.

5 N. M. Karayannis, L. L. Pytlewski and C. M. Mikulski, *Coord. Chem. Rev.*, *11*, 93 (1973).

6 W. H. Watson, *Inorg. Chem.*, *8*, 1879 (1969).

7 Y. Muto, M. Kato, H. B. Jonassen and H. N. Ramaswamy, *Bull. Chem. Soc. Japan*, *40*, 1535 (1967); M. Kato, Y. Muto and H. B. Jonassen, *ibid.*, *40*, 1738 (1967); Y. Muto, M. Kato, H. B. Jonassen and K. Kakiuchi, *ibid.*, *41*,

1495 (1968); Y. Muto, M. Kato, H. B. Jonassen and L. C. Cusachs, *ibid., 42,* 417 (1969).

8 G. Costa and E. Pauluzzi, *Univ. Stud. Trieste, Fac. Sci., Ist. Chim., Pubbl. 12* (1956); *Chem. Abstr., 51,* 4823b (1957).

9 Y. Kakiuti, S. Kida and J. V. Quagliano, *Spectrochim. Acta, 19,* 201 (1963); L. C. Nathan and R.O. Ragsdale, *Inorg. Chim. Acta, 10,* 177 (1974).

10 M. Zackrisson and I. Lindqvist, *J. Inorg. Nucl. Chem., 17,* 69 (1961).

11 P. W. N. M. van Leeuwen and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas, 87,* 86 (1968).

12 V. M. Ellis, R. S. Vagg and E. C. Watton, *J. Inorg. Nucl. Chem., 36,* 1031 (1974).

13 J.-P. Deloume, R. Faure and H. Loiseleur, *Acta Crystallogr., B33,* 2709 (1977).

14 A. D. van Ingen Schenau, W. L. Groeneveld and J. Reedijk, *Spectrochim. Acta, 30A,* 213 (1974); A. D. van Ingen Schenau, C. Romers, D. Knetsch and W. L. Groeneveld. *ibid., 33A,* 859 (1977).

15 A. T. Hutton and D. A. Thornton, *J. Mol. Struct., 39,* 33 (1977).

16 R. J. H. Clark and C. S. Williams, *Inorg. Chem., 4,* 350 (1965); R. J. H. Clark, *Spectrochim. Acta, 21,* 955 (1965).

17 N. M. Karayannis, C. M. Mikulski, M. J. Strocko, L. L. Pytlewski and M. M. Labes, *J. Inorg. Nucl. Chem., 33,* 3185 (1971).

18 D. Bryson and R. H. Nuttall, *Spectrochim. Acta, 26A,* 2275 (1970); P. Bamfield, R. Price and R. G. J. Miller, *J. Chem. Soc. A,* 1447 (1969).

19 R. Whyman and W. E. Hatfield, *Inorg. Chem., 6,* 1859 (1967).

20 W. Byers, A. B. P. Lever and R. V. Parish, *Inorg. Chem., 7,* 1835 (1968).

21 R. S. Sager, R. J. Williams and W. H. Watson, *Inorg. Chem., 8,* 694 (1969).

22 H. H. Jaffé, *J. Am. Chem. Soc., 77,* 4451 (1955); L. R. Caswell, F. C. Lee and L. T. Creagh, *J. Heterocycl. Chem., 9,* 551 (1972).

23 W. Byers, B. Fa-Chun Chou, A. B. P. Lever and R. V. Parish, *J. Am. Chem. Soc., 91,* 1329 (1969).

24 J. H. Nelson, R. G. Garvey and R. O. Ragsdale, *J. Heterocycl. Chem., 4,* 591 (1967).

25 D. J. Hodgson, *Progress in Inorg. Chem., 19,* 173 (1975).

26 W. J. Geary, *Coord. Chem. Rev., 7,* 81 (1971).

27 G. W. Inman Jr., J. A. Barnes and W. E. Hatfield, *Inorg. Chem., 11,* 764 (1972); G. W. Inman, Jr., and W. E. Hatfield, *ibid., 11,* 3085 (1972).

28 H. W. Richardson, W. E. Hatfield, H. J. Stoklosa and J. R. Wasson, *Inorg. Chem., 12,* 2051 (1973); H. W. Richardson, J. R. Wasson, W. E. Hatfield, E. V. Brown and A. C. Plasz, *ibid., 15,* 2916 (1976); H. W. Richardson and W. E. Hatfield, *J. Am. Chem. Soc., 98,* 835 (1976).

29 D. E. Chasan, L. L. Pytlewski, C. Owens and N. M. Karayannis, *J. Inorg. Nucl. Chem., 40,* 1019 (1978).

30 A. Kleinstein and G. A. Webb, *J. Inorg. Nucl. Chem., 33,* 405 (1971).