BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 1654—1655(1972)

An ESR Study of Some Substituted Pyridine *N*-Oxide Copper(II) Complexes

Derek P. FREYBERG, Toshiyuki ISOBE, and Seizo MISUMI
Inorganic Chemistry Laboratory, Faculty of Science, Kyushu University, Fukuoka

(Received December 6, 1971)

The ESR (methanol solution, frozen solution, powder, and single crystal) spectra of $[CuL_4](ClO_4)_2$, where L=pyridine *N*-oxide, α-picoline *N*-oxide, β-picoline *N*-oxide, γ-picoline *N*-oxide, and 2,6-lutidine *N*-oxide, and of $[CuL_6](ClO_4)_2$, where L=pyridine *N*-oxide and γ-picoline *N*-oxide, have been obtained. The preparation of hexa(γ-picoline *N*-oxide) copper(II) perchlorate is reported. The solution and frozen solution spectra indicate a very similar bonding in all the complexes, with moderately ionic metal-oxygen. The powder spectra reveal all the tetrakis complexes to be axially symmetric; though tetra(γ-picoline *N*-oxide) copper(II) perchlorate shows a reversal of the usual order of the *g*-values. This is explained in terms of the packing interactions within the crystal structure, rather than metal-ligand interaction. All the single crystal spectra are characteristic of axially symmetric complexes. Hexa(pyridine *N*-oxide)copper(II) perchlorate gives an isotropic ESR spectrum, but this does not seem to be due to exchange interaction. Hexa(γ-picoline *N*-oxide)copper(II) perchlorate gives an axial ESR spectrum with a considerable tetragonal misalignment.

Although there has been considerable interest in transition metal complexes with aromatic amine *N*-oxides (particularly pyridine *N*-oxide) in recent years,[1] the principal interest lies in copper(II) in binuclear complexes formed with *e.g.* $CuCl_2$. We report here the ESR (methanol solution, frozen methanol solution (−150°C), powder, and single crystal) spectra of $[CuL_4](ClO_4)_2$ where L=pyridine *N*-oxide (pyNO), α-picoline *N*-oxide (αNO), β-picoline *N*-oxide (βNO), γ-picoline *N*-oxide (γNO), and 2,6-lutidine *N*-oxide (lNO); and $[CuL_6](ClO_4)_2$ where L=pyNO and γNO. The preparation of $[Cu(\gamma NO)_6](ClO_4)_2$ is reported for the first time.

Experimental

The aromatic amine *N*-oxide ligands were prepared from the amines by the method of Ochiai.[2] The chloroform extract, after removal of the chloroform by rotary evaporation, was used without further purification. The copper(II) complexes were prepared by the usual methods.[3,4] $[Cu(\gamma NO)_6](ClO_4)_2$ was prepared by the reaction of hot acetone[5] solutions of $Cu(ClO_4)_2 \cdot 6H_2O$ and γNO in 1:20 mole ratio. On cooling, pale lime-green needles separated. They were filtered off, washed with acetone and dried over silica gel. If the filtrate is allowed to stand further, dark green crystals of $[Cu(\gamma NO)_4](ClO_4)_2$ and not $[Cu(\gamma NO)_6](ClO_4)_2$ are formed. Analysis: found C; 47.2, H; 4.61, N; 9.18%; calcd for $CuC_{36}H_{42}N_6O_{14}Cl_2$ C; 47.1, H; 4.61, N; 9.19%.

Reflection spectra of powdered samples and absorption spectra were taken on Hitachi EPS-3T and EPS-2 spectrophotometers, respectively. ESR spectra were taken on a JEOL JES ME-3X spectrometer with a variable temperature attachment operating at about 9.3 GHz. Calibration was made with a Mn^{2+}/MgO powder standard ($g_4 = 1.981$). Solutions for absorption and ESR measurements were approximately 1: 20 Cu: L in MeOH. Single crystal spectra were taken on a holder similar to that described by Hathaway and Billing,[6] except that it was made of silica rod. The same face of the crystal can be mounted (using silicone grease) onto two mutually perpendicular faces of the rod, and the rod rotated in the spectrometer cavity. The crystal was thus rotated about three orthogonal axes, and spectra were taken every 15° in each rotation.

Results

The *g*- and *A*-values obtained from ESR spectra of the solution and frozen solution samples together with absorption maxima of the solutions are shown in Table 1.

The lNO spectra show a rather large $g_{\parallel}$ and A^*, but a low g^*. This might be due to steric interaction involving the methyl groups of ligand molecules. The value of α^2, a measure of the covalency of the metal-ligand bond,[7] changes very little indicating that the bonding in all cases is similar.

---

[1] R. G. Garvey, J. H. Nelson, and R. G. Ragsdale, *Coordin. Chem. Rev.*, **3**, 375 (1968).

[2] E. Ochiai, *J. Org. Chem.*, **18**, 534 (1953).

[3] J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley, and S. Y. Tyree, *J. Amer. Chem. Soc.*, **83**, 3770 (1961).

[4] R. L. Carlin, *ibid.*, **83**, 3773 (1961).

[5] S. J. Gruber, C. H. Harris, E. Kokot, S. T. Lenzer, T. N. Lockyer, and E. Sinn, *Aust. J. Chem.*, **20**, 2403 (1967).

[6] B. J. Hathaway and D. E. Billing, *Coordin. Chem. Rev.*, **5**, 143 (1970).

[7] V. C. Swett and E. P. Dudek, *J. Phys. Chem.*, **72**, 1244 (1968).

TABLE 1. SOLUTION AND FROZEN SOLUTION SPECTRA

Ligand	$g_\parallel$	g^*	$g_\perp$	$A_\perp$(G)	A^*(G)	$A_\perp$(G)	ΔE(cm^{-1})	α^2
pyNO	2.320	2.160	2.080	138	52	9	12700	0.84
αNO	2.291	2.151	2.081	150	52	3	12300	0.86
βNO	2.300	2.161	2.082	150	60	15	12500	0.82
γNO	2.297	2.152	2.080	155	60	12	13200	0.86
lNO	2.393	2.126	2.043	149	80	45	12500	0.79

Notes: 1. $g_\perp=1/2(3g^*-g_\parallel)$; $A_\perp=1/2(3A^*-A_\parallel)$.
2. $g_\parallel$, $g^*\pm0.005$; $A_\parallel$, $A^*\pm3$G; $\Delta E\pm50$ cm^{-1}
3. Samples: $Cu(ClO_4)_2$+ligand 1:20 in MeOH at 25°C and −150°C.

TABLE 2. POWDER SPECTRA

Sample	$g_\parallel$	$g_\perp$	G	ΔE(cm^{-1})
$[Cu(pyNO)_4](ClO_4)_2$	2.240	2.065	3.7	14700
$[Cu(\alpha NO)_4](ClO_4)_2$	2.261	2.061	4.4	14900
$[Cu(\beta NO)_4](ClO_4)_2$	2.282	2.065	4.3	14500
$[Cu(\gamma NO)_4](ClO_4)_2$	2.066	2.172	—	14700
$[Cu(lNO)_4](ClO_4)_2$	2.241	2.054	4.5	15600
$[Cu(pyNO)_6](ClO_4)_2$	Isotropic	g=2.189	—	12300/9600sh
$[Cu(\gamma NO)_6](ClO_4)_2$	2.313	2.102	3.1	13000/10500sh

Notes : 1. $g_\parallel$, $g_\perp\pm0.005$; $\Delta E\pm50$ cm^{-1}
2. $G=(g_\parallel-2)/(g_\perp-2)$

The *g*-values obtained from ESR spectra of the powder samples together with reflection maxima of the complexes are shown in Table 2.

All the spectra are characteristic of axial symmetry[6] and the values of $g_\parallel$ and $g_\perp$ were obtained by the method of Kneubühl.[8] For the tetrakis complexes, the single crystal *g*-values were identical with the powder *g*-values within experimental error. The spectrum of $[Cu(\gamma NO)_6](ClO_4)_2$, despite analytical purity of the sample, displayed lines due to $[Cu(\gamma NO)_4](ClO_4)_2$ present as an impurity as well as to the hexakis complex. However, the *g*-value assignments were confirmed by the spectrum of $[Cu(\gamma NO)_6](ClO_4)_2$ diluted 1: 500 in $[Zn(\gamma NO)_6](ClO_4)_2$, which gave $g_\parallel=2.326$, $A_{11}=110$ G, $g_\perp=2.087$, and $A_\perp=30$ G. The usual reason for the observation of an isotropic spectrum, as for $[Cu(pyNO)_6](ClO_4)_2$, is that the tetragonal axes are grossly misaligned. Exchange coupling[9] between local copper(II) ions does not seem to occur, as the spectrum of $[Zn(pyNO)_6](ClO_4)_2$ containing 1% Cu^{2+} is identical with that of the undiluted complex.

Discussion

The solution and frozen solution spectra display no unusual features; the ESR and solution spectra are very similar for all the complexes. Thus we can state that the bonding within a single unit is identical for all the complexes.

The powder spectra, on the other hand, show an unexpected feature, *viz.*, $g_\perp$ is greater than $g_\parallel$ for $[Cu(\gamma NO)_4](ClO_4)_2$ and not for any of the other complexes. The value of $G(=g_\parallel-2/g_\perp-2)$ has been used[9] to explain distortions from tetragonal symmetry. The result $G>4.0$ indicates good alignment of the tetragonal axes within the crystal, and $G<4.0$ indicates misalignment. Thus the αNO, βNO, and lNO complexes show aligned tetragonal axes and the pyNO complex shows misaligned ones. G has no meaning in the case where $g_\perp$ is greater than $g_\parallel$. Single crystal spectra of all the complexes followed the theoretical pattern for a complex with axial symmetry[10] *i.e.* $g^2=g_\perp^2 \sin^2\theta+g_\parallel^2 \cos^2\theta$ for rotations about two axes and $g=g_\perp$ for rotation about the third axis. These spectra confirmed the assignments of $g_\parallel$ and $g_\perp$ for the tetrakis complexes.

The reflection spectra of the five tetrakis complexes are all similar, and it is likely that the crystal environment is also similar. Hence, a reversal of the *g*-values for $[Cu(\gamma NO)_4](ClO_4)_2$ is unexpected. Usually, a value of $g_\perp$ greater than $g_\parallel$ indicates a $d_z{}^2$ ground state;[11] however, this gives a $g_\parallel$ close to the free electron value (g=2.002). In the present case, $g_\parallel=2.066$, a value considerably higher than is usual for $d_z{}^2$. Also, a $d_z{}^2$ ground state does not favour square planar coordination and is usually observed in trigonal complexes. For these reasons, and also because the solution and frozen solution spectra are similar to those of the other complexes, we conclude that the reversal of the *g*-values is not in the metal atom environment but in the crystal packing. This is supported by examination of structural models based on the crystal structure of $[Cu(pyO)_4](ClO_4)_2$ which has been described by Lee *et al.*[12] These models indicate that a methyl group in the α- or β-position does not significantly alter the size of the complex unit but γ-substitution does. It may be noted also, that the ESR spectrum of Cu^{2+} in $[Pd(\gamma NO)_4](ClO_4)_2$ is normal *i.e.* $g_\parallel>g_\perp$.

---

[8] F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1960).

[9] I. M. Procter, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc. A*, **1968**, 1678.

[10] R. M. Golding, "Applied Wave Mechanics", Van Nostrand, London, (1969).

[11] B. J. Hathaway and A. A. G. Tomlinson, *Coordin. Chem. Rev.*, **5**, 1 (1970).

[12] J. D. Lee, D. S. Brown, and B, G. A. Melsom, *Acta Crystallogr.*, **B25**, 1378 (1969).