

4-Substituted Quinoline N-Oxide Complexes of Copper(II) Acetate¹

J. J. MacDOUGALL^{2a,b}, L. C. NATHAN^{2c} and J. H. NELSON^{2b}

Departments of Chemistry, University of Nevada, Reno, Nevada 89507, and the University of Santa Clara, Santa Clara, California 95053, U.S.A.

Received September 1, 1975

A series of 4-substituted quinoline N-oxides (4ZQNO) and isoquinoline N-oxide (IQNO) have been found to react with copper(II) acetate to form the dimeric complexes $[\text{Cu}(\text{CH}_3(\text{COO})_2 \cdot 4\text{ZQNO})_2 \cdot n\text{H}_2\text{O}]$ where Z is CH_3O , CH_3 , H and Cl. The complexes were characterized by elemental analyses, electronic and infrared spectra and magnetic measurements. These data are all consistent with the δ -bonding model. The contributions of ligand steric effects and σ - and π -bonding strengths to the magnitude of the copper-copper interaction are discussed. The isoquinoline N-oxide complex dehydrates over a period of time, resulting in crystal degradation to a powder. This is accompanied by a structural reorganization wherein the acetate groups probably change from bridging to monodentate. This results in a change in the magnetic moment from $\mu = 1.34$ B.M. to $\mu = 2.00$ B.M. with time.

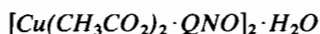
Introduction

Numerous studies³ have been conducted on dimeric transition metal carboxylate complexes of the type $[\text{M}(\text{RCO}_2)_2\text{L}]_2$ because of the interest in metal-metal bonds. There are three independent factors subject to variation within these series of complexes, and their resultant influence on the strength of the metal-metal interaction may be assessed as these are changed. The metal, M, has been the subject of several investigations, while the ligand, L, and the substituent, R, have been widely varied. We^{3a} previously found that the copper(II) acetate complexes of 4-substituted pyridine N-oxides exhibited a regular trend between the magnitude of the copper-copper interaction and the basicity of the pyridine N-oxide. The magnitude of this interaction increased as the basicity of the ligand decreased. This was attributed to π -back bonding.^{3a} Since it has previously been shown that quinoline N-oxides are better⁴ π -back bonding ligands than the analogous pyridine N-oxides, it was of interest to examine copper(II) acetate complexes with the 4-substituted quinoline N-oxides. As this study was being completed we became aware of a similar though less detailed investigation.^{3b-d} Where overlap occurs, there is good agreement among these works.

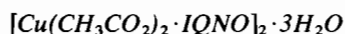
Experimental

Synthesis

The ligands were synthesized as previously described^{4a} and purified by vacuum distillation or recrystallization from acetone immediately prior to use. The complexes were each prepared in two ways. An example of each is given below.



A suspension of 5 g (1.25×10^{-2} mol) copper(II) acetate monohydrate and 9.1 g (6.27×10^{-2} mol) quinoline N-oxide in 100 ml of 95% ethanol, 10 ml 2,2-dimethoxypropane and a few drops of glacial acetic acid was heated for 30 minutes or until dissolution was essentially complete. This solution was filtered hot and allowed to cool to room temperature, at which time large green crystals volunteered. These were filtered, washed with anhydrous diethyl ether and vacuum dried at room temperature to yield 5.6 g (64%) $[\text{Cu}(\text{OAc})_2 \cdot \text{QNO}]_2 \cdot \text{H}_2\text{O}$.



Twenty-five ml of 2,2-dimethoxypropane was added to a solution containing 0.732 g (1.83×10^{-3} mol) copper(II) acetate in 250 ml boiling anhydrous methanol. To this blue solution was added 1.332 g (9.19×10^{-3} mol) isoquinoline N-oxide in 25 ml methanol plus 10 ml 2,2-dimethoxypropane. The resultant green solution was concentrated to approximately 150 ml, filtered to remove unreacted copper(II) acetate and cooled to room temperature. Anhydrous diethyl ether was added to this solution to initiate precipitation. The green microcrystalline precipitate was filtered, washed with anhydrous diethyl ether and vacuum dried at room temperature over phosphorus pentoxide to yield 0.95 g (73%) $[\text{Cu}(\text{OAc})_2 \cdot \text{IQNO}]_2 \cdot 3\text{H}_2\text{O}$.

Carbon, hydrogen and nitrogen analyses were performed by Chemalytics, Inc., Tempe, Arizona. Copper analyses were obtained using EDTA.⁵ The data are listed in Table I.

Physical Measurements

Electronic spectra were run on nujol mull suspensions (the complexes) or 40% sulfuric acid in ethanol solu-

TABLE I. Elemental Analyses and Decomposition Points for the Complexes $[\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{L}]_2$.

L	D.p. °C	%C		%H		%N		%Cu	
		Calc.	(Found)	Calc.	(Found)	Calc.	(Found)	Calc.	(Found)
4CH ₃ OQNO ^b	195–200	47.17	(46.90)	4.21	(4.06)	3.92	(3.66)	16.95	(16.75)
4CH ₃ QNO	197–200	49.36	(49.69; 49.67)	4.40	(4.51; 4.42)	4.11	(4.10)	18.64	(18.98)
QNO ^c	203–206	46.51	(46.87; 46.84)	4.17	(3.91; 4.02)	4.17	(4.14)	18.93	(19.44)
4ClQNO	208–211	43.24	(42.95)	3.32	(3.23)	3.88	(3.74)	17.58	(17.57)
IQNO ^d	203–207	44.15	(43.66)	4.52	(4.76)	3.96	(3.91)	17.97	(17.98)
IQNO ^b	195–200	45.30	(45.64)	4.35	(4.40)	4.06	(4.14)	–	–

^a All complexes are green. ^b Dihydrate. ^c Monohydrate. ^d Trihydrate.

TABLE II. Electronic Spectral Data for the Complexes $[\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{L}]_2$.

L	Band I (kK)	Band II (kK)	¹ L _a + ¹ L _b (kK)		¹ B _b (kK)	
			Ligand H ⁺		Complex	
			Ligand H ⁺	Complex	Ligand H ⁺	Complex
4CH ₃ OQNO	13.99	28.17	31.85	36.76	44.84	40.00
4CH ₃ QNO	13.76	28.82	30.96, 31.75	32.05	38.17	44.44
QNO	13.99	28.82	31.20, 32.40	33.67	42.90	41.15
4ClQNO	14.18	28.17	31.25	31.55	37.03	41.32
IQNO ^a	13.57	29.59	35.71, 31.30, 30.21	33.33	44.44	38.91
IQNO ^b	13.95	28.41	35.61, 31.30, 30.21	33.33	44.44	38.91

^a Trihydrate. ^b Dihydrate.

TABLE III. Magnetic Data for the Complexes $[\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{L}]_2$.

L	10 ⁶ χ _g (cgsu)	10 ⁶ χ _m (cgsu)	10 ⁶ χ _m ' (cgsu)	T (°K)	μ _{eff} B.M.	pK _a ^d
4CH ₃ OQNO	1.89	708	881	295	1.39	1.62
4CH ₃ QNO	1.94	661	817	296	1.34	1.44
QNO	2.25	736	880	295	1.40	0.86
4ClQNO	1.76	636	797	296	1.33	0.47
IQNO ^a	1.83	647	811	297	1.34	1.01
IQNO ^b	2.25	796	900	293	1.47	1.01
IQNO ^c	4.51	1596	1699	293	2.00	1.01

^a Fresh sample, trihydrate dimer. ^b Sample one month old, dihydrate dimer. ^c Sample seven months old, monohydrate monomer. ^d Reference 3a.

tions (the ligands) using Beckman DB-GT and Cary 14 recording spectrophotometers. The results are given in Table II.

The magnetic moments were determined by the Gouy technique at 7K Gauss. The compound Hg[Co(SCN)₄] was used as a calibrant. The diamagnetic corrections were calculated from Pascal's constants. The effective magnetic moments were calculated using the expression $\mu_{\text{eff}} = 2.839 [(\chi_m' - N_\alpha)T]^{1/2}$, where N_α represents the temperature-independent paramagnetism associated with the copper ion; a value of $N_\alpha = 60 \times 10^{-6}$ cgsu being used. The results listed in Table III are the averages of three independent measurements on different samples from at least two separate

preparations with a maximum variance of ± 0.03 Bohr magnetons in the derived magnetic moments.

Infrared spectra of the ligands and their complexes as nujol mulls were obtained in the 4000–600 cm⁻¹ region on a Beckmann IR-8 recording spectrometer and were calibrated with known frequency bands of polystyrene. The data are listed in Table IV.

Decomposition points were determined with a Mel-temp melting point apparatus and are uncorrected.

Results and Discussion

The elemental analyses indicate that the complexes have the formula $[\text{Cu}(\text{CH}_3\text{CO}_2)_2 \cdot \text{L}] \cdot n\text{H}_2\text{O}$. Except

TABLE IV. Infrared Spectral Data for the Complexes $[\text{Cu}(\text{OAc})_2 \cdot \text{L}]_2$.

L	State	ν_{NO}^a	$\Delta\nu_{\text{NO}}$	$\nu_{\text{COO}}(\text{assym})$	$\nu_{\text{COO}}(\text{sym})$	δ_{NO}	$\Delta\delta_{\text{NO}}$
4CH ₃ OQNO	Nujol	1288	-8	1618	1441 1434 sh	832	-10
4CH ₃ QNO	Nujol	1208	-2	1623 1616 sh	1434 1416 sh	844	-21
QNO	Nujol	1238 1225	-3	1618	1429	805 797 sh	-13
4ClQNO	Nujol	1300 1256	0	1616	1437	840	-16
IQNO ^b	Nujol	1180	+2	1618	1428	822	-4
IQNO ^b	KBr	1178	+4	1619	1425	821	-3
IQNO ^c	Nujol	1168	+14	1610	1417	815	-11
IQNO ^c	KBr	1167	+15	1614	1415	814	-10

^a Frequencies and frequency shifts are in cm^{-1} . For the free N-oxide frequencies, see H. Shindo, *Chem. Pharm. Bull. (Tokyo)*, 8, 845 (1960). The carboxylate frequencies were assigned as before.^{2a} $\Delta\nu_{\text{NO}} = \nu_{\text{NO}} \text{ free ligand} - \nu_{\text{NO}} \text{ complex}$, $\Delta\delta_{\text{NO}} = \delta_{\text{NO}} \text{ free ligand} - \delta_{\text{NO}} \text{ complex}$. ^b Trihydrate. ^c Dihydrate.

for the isoquinoline N-oxide complex they are all hygroscopic, as are their pyridine N-oxide analogs.³ Their structure is established as that of the parent dimeric copper(II) acetate monohydrate, as evidenced by the frequencies of ν_{COO} , ν_{NO} ; the magnitude of the magnetic moments μ_{eff} , and the presence of the 28–29 kK band in their electronic spectra (Tables II–IV). For all cases except isoquinoline N-oxide, ν_{NO} , the nitrogen–oxygen stretching frequency was the same as that of the free ligand or shifted slightly to higher energy. For isoquinoline N-oxide, ν_{NO} shifts to lower energy upon complexation. We anticipated a shift to lower energy for two reasons, the first being a simple mass effect and the second being a lowering of the nitrogen–oxygen bond order. This occurred in the complexes of pyridine N-oxides with copper(II) acetate, where shifts of 25–49 cm^{-1} were observed.^{3a} When quinoline N-oxides interact with methanol and only a σ -bond is formed, ν_{NO} shifts to lower energy⁶ by 4–28 cm^{-1} . Collectively, these facts are consistent with the existence of metal-to-ligand π -back donation, as was previously found for the Co(II) and Ni(II) complexes of quinoline N-oxides.⁴ The correlation between ν_{NO} and σ_{pyNO} that was apparent for the pyridine N-oxide complexes^{3a} is not evidenced for the quinoline N-oxide complexes. This is most likely due to the fact that ν_{NO} is not a pure vibration in the quinoline N-oxides.⁷

When the copper(II) acetate complexes of 4-substituted pyridine N-oxides were investigated,³ it was argued that π -back bonding plays an important role in determining the magnitude of the copper–copper interaction. The quinoline N-oxides are slightly stronger bases^{4a} than the pyridine N-oxides indicating a greater ability to σ -bond. The second aromatic ring in the quinoline N-oxide system increases its ability to delocalize electrons relative to pyridine N-oxide, resulting in

a greater capacity for π -back bonding.⁴ The greater steric bulk of the quinoline N-oxides should reduce the σ donor ability relative to the pyridine N-oxides. For corresponding complexes then, if basicity (σ) effects predominate, the effective magnetic moments of the quinoline N-oxide complexes should be greater than those of the pyridine N-oxide complexes. If, on the other hand, steric or π -electronic effects predominate, these effective magnetic moments should be smaller than for the pyridine N-oxide complexes. As shown in Figure 1 there is a general trend in the magnetic susceptibility with basicity for both series of complexes where χ_m' decreases as the basicity decreases. Since π -bonding should decrease with increasing internuclear distance more rapidly than sigma bonding, the fact that the quinoline N-oxide complexes have magnetic moments similar to the pyridine N-oxide complexes implies that π -bonding is important for these complexes.

The electronic spectral data (Table II) support this contention. In this table the intraligand transitions ($'L_a$, $'L_b$ and $'B_b$) of the complexes are compared with those of the protonated ligands. Were only σ -interactions occurring, these spectra should be very similar since the transitions are essentially ring π - π^* and n - π^* transitions and not isolated N–O moiety transitions.⁸

An interesting note concerns the isoquinoline N-oxide complex. Even though the basicity of isoquinoline N-oxide is greater and the steric hindrance less than that of quinoline N-oxide, the magnetic susceptibility of the isoquinoline N-oxide complex is less than that of the quinoline N-oxide complex. Over a period of time, dehydration takes place, resulting in degradation of the crystalline complex to a powder. As this occurs, the magnetic susceptibility gradually increases from 1.34 B.M. for the freshly prepared sample (trihydrated) to 2.00 B.M. for a seven-month-old sample.

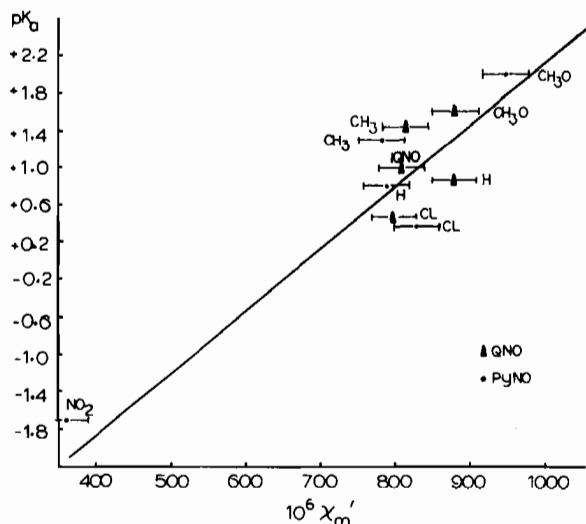


Figure 1. Plot of pK_a for the dissociation^{3a} of HL^+ versus $10^6 \chi_m'$ for the complexes $[Cu(CH_3CO_2)_2 \cdot L]_2$. (·) $L = 4ZpyNO$, (\blacktriangle) $L = 4ZQNO$.

This reaction is intriguing, as usually N-oxide complexes are hygroscopic.⁹ Changes are also evident in the electronic and infrared spectra (Table II and IV). All these data are consistent with a structural reorganization upon dehydration. It has been previously noted¹⁰ that monomeric pseudo-tetrahedral complexes of copper(II) having oxygen donors with similar sizes and basicities to the amine oxides, such as $CuCl_2[(C_6H_5)_3AsO]_2$ and $CuBr_2[(C_6H_5)_3PO]_2$, exhibit effective magnetic moments in the neighborhood of 2.00 B.M. The N-oxide bridged complex $[CuCl_2(4-NO_2-C_9H_6NO)]_2$ exhibits a moment of 1.99 B.M.¹⁰ In copper(II) complexes of malonic acid, the effective magnetic moment increases as the number of coordinated water molecules increases.⁶ One could then account for the data on the isoquinoline N-oxide complex by a time-dependent rearrangement involving a change from a dimeric form to some form of monomeric structure, the exact nature of which must await X-ray analysis.

Conclusions

By comparing the data for the quinoline N-oxide series of complexes to that obtained for the pyridine N-oxide series,^{3a} one can make the following conclusions. Even though the basicities of the two series of ligands differ somewhat⁴ their donor abilities toward copper(II) acetate are similar, as is true for cobalt(II) and nickel(II) complexes. Since there are greater steric effects in the quinoline N-oxide series than in the pyridine N-oxide series, this suggests that there is a greater amount of π -back bonding in the quinoline N-oxide complexes than in the pyridine N-oxide complexes. Thus, the magnetic susceptibilities, χ_m' , for both series of ligands follow the same trend with pK_a ,⁴

that is, as the basicity increases χ_m' increases regularly, as exhibited in Figure 1. Consequently, π -back bonding seems to be more important in determining the magnitude of the metal-metal interaction than steric effects.

Steric effects are nonetheless observable and might explain the behavior of the isoquinoline N-oxide complex, which apparently changes crystal structure with time. These are crystal packing force effects (steric effects in the crystal lattice) rather than steric effects on the metal-ligand interaction, as isoquinoline N-oxide should possess less steric interaction at the donor site and greater steric interaction in the lattice than Quinoline N-oxide.

These data are all consistent with the δ -bonding model for the metal-metal interaction and suggest that the strength of this interaction increases as the electron density at copper decreases. Thus, by π -back donation into the N-oxide π antibonding orbitals, electron density is being removed from orbitals which are essentially copper-copper antibonding in character.

Acknowledgements

We are pleased to acknowledge the financial support of the University of Nevada, Reno, Research Advisory Board. Helpful discussions with Professor D. J. Hodgson are gratefully acknowledged.

References

- Presented in part at the 30th Annual Northwest Regional Meeting of the American Chemical Society, Honolulu, Hawaii, June 12-13, 1975. See abstract No. 162.
- a) Undergraduate Research Participant, University of Santa Clara;
b) University of Nevada, Reno;
c) University of Santa Clara.
- a) D. Hibdon and J. H. Nelson, *Inorg. Chim. Acta*, **7**, 629 (1973) and references contained therein.
b) J. Kohout and J. Krátsmař-Smogrovic, *Chem. Zvesti*, **22**, 481 (1968).
c) J. Krátsmař-Smogrovic and M. Zemlicka, *Z. Naturforsch.*, **28b**, 689 (1973).
d) S. J. Gruber, C. M. Harris, E. Kokot, S. L. Lenzer, T. N. Lockyer and E. Sinn, *Aust. J. Chem.*, **20**, 2403 (1967).
- a) J. H. Nelson, L. C. Nathan and R. O. Ragsdale, *Inorg. Chem.*, **7**, 1840 (1968).
b) R. W. Kluiber and W. De W. Horrocks, Jr., *J. Am. Chem. Soc.*, **88**, 1399 (1966).
- F. J. Welcher, "The Analytical Uses of Ethylenediaminetetraacetic Acid", Van Nostrand, New York, N. Y., 1957, p. 242.
- R. Whyman, W. E. Hatfield and J. S. Paschal, *Inorg. Chim. Acta*, **1**, 113 (1967).
- H. Shindo, *Chem. Pharm. Bull. (Tokyo)*, **8**, 845 (1960).
- E. Ochiai, "Aromatic Amine Oxides", Elsevier, New York, N. Y., 1967, pp. 132-167.
- R. G. Garvey, J. H. Nelson and R. O. Ragsdale, *Coordin. Chem. Rev.*, **3**, 375 (1968).
- M. Kato, H. B. Jonassen and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).