Binuclear Copper(II) Complexes bridged by Oxamidate and Dithio-oxamidate Groups. Synthesis, Structure, and Magnetism†

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Binuclear copper(II) complexes bridged by oxamidate (oxd) or dithio-oxamidate (dto) groups $[Cu_2L_2(oxd)]X_2$ and $[Cu_2L_2(dto)]X_2$ [L = 2,2′-bipyridyl (bipy) or 1,10-phenanthroline, X = NO_3 or ClO_4], have been synthesized. Single-crystal *X*-ray analysis for $[Cu_2(bipy)_2(oxd)][ClO_4]_2\cdot 2dmf$ (dmf = dimethylformamide) reveals that the oxd^{2-} ion in *trans* conformation bridges two copper(II) ions with an intermetal distance of 5.192(2) Å. The configuration around each copper is square pyramidal with two nitrogens of bipy and one nitrogen and one oxygen of oxd in the basal plane and a perchlorate oxygen at the apex [2.433(9) Å]. The dto-bridged complexes are characterized by two intense i.r. bands at 1 540 and 1 440 cm^{-1} and a charge-transfer band at (21.6—21.9) × 10^3 cm^{-1}. Magnetic analyses in the temperature range 80—300 K on the basis of the Bleaney–Bowers equation gave $-2J$ values (singlet–triplet energy separation) of 488—566 cm^{-1} for the oxd-bridged complexes and 726—982 cm^{-1} for the dto-bridged complexes, indicating that the dithio-oxamidate bridge mediates a stronger antiferromagnetic spin exchange between copper(II) ions than does the oxamidate bridge. Cyclic voltammograms for the oxd complexes show an irreversible couple at +0.1 V *vs.* the saturated calomel electrode which is assigned to the process $Cu^{II}_2 \longrightarrow Cu^{I}Cu^{II}$.

Studies of magnetic spin exchange in polynuclear metal complexes in terms of stereochemical factors and the nature of bridging groups are of current interest.[1] In particular, the exploitation of new bridging systems which can mediate a strong antiferromagnetic spin exchange between paramagnetic ions is directed towards the development of ferrimagnetic materials.[2]

It is known that oxalate (ox) functions as a bridge between two copper(II) ions.[3—8] The spin-exchange interaction mediated through this bridge in such complexes depends highly upon the geometry around the metal ion,[7] and a strong antiferromagnetic spin exchange occurs when the oxalate group co-ordinates to the equatorial sites of two copper(II) ions. Large singlet–triplet energy separations ($-2J$) have been reported for $[Cu_2(tmen)_2(H_2O)_2(ox)]^{2+}$ (tmen = *N,N,N′,N′*-tetramethylethylenediamine) (385.4 cm^{-1})[5] and $[Cu_2(bipy)_2(H_2O)_2(ox)]^{2+}$ (bipy = 2,2′-bipyridyl) (385.9 cm^{-1}).[6] Some oxamidate(oxd)-bridged binuclear copper(II) complexes are also known[3,9—12] and it is suggested that the oxamidate bridge can mediate a stronger antiferromagnetic spin exchange than the oxalate bridges.[3,12] Dithio-oxamidate (dto) ion generally forms polynuclear complexes with various metal ions, but no binuclear copper(II) complex has been obtained so far. The only available examples are those of dithio-oxamide derivatives[13—15] with chelating arms attached to the amide nitrogens.

In order to assess comparatively the effects of oxamidate and dithio-oxamidate bridges upon the spin exchange between copper(II) ions, it was necessary to synthesize a series of binuclear complexes of essentially the same structure except for the bridging group. In this study we have obtained oxd- and dto-bridged binuclear copper(II) complexes, $[Cu_2L_2(oxd)]X_2$ and $[Cu_2L_2(dto)]X_2$, where L is bipy or 1,10-phenanthroline (phen) acting as the 'end-cap' ligand and X is nitrate or perchlorate ion. This paper reports the synthesis, *X*-ray crystal-structure analysis, and cryomagnetic, spectral, and electrochemical properties of the complexes.

Experimental

Materials.—2,2′-Bipyridyl, phen, oxamide, and dithio-oxamide were purchased from Tokyo Kasei Chemical Co. The complexes $[Cu(bipy)_2]X_2$ and $[Cu(phen)_2]X_2$ (X = NO_3 or ClO_4) were obtained by the literature methods.[16] Methanol, dimethylformamide (dmf), and tetrahydrofuran (thf) as solvents were purified and dried in the usual ways.

Preparations.—The oxd-bridged complexes (**1**)—(**4**) (see Table 1) were obtained in nearly the same way as exemplified below. To a stirred suspension of $[Cu(bipy)_2][NO_3]_2$ (500 mg) and H_2oxd (44 mg) in absolute methanol (25 cm^3) was added LiOH powder (30 mg) little by little with stirring. A deep blue solution was formed, from which blue microcrystals separated. They were collected by filter suction and recrystallized from dmf.

The dto-bridged complexes (**5**)—(**7**) were obtained by two different ways as exemplified below.

Method 1. A mixture of $[Cu(bipy)_2][ClO_4]_2$ (575 mg) and H_2dto (60 mg) in absolute methanol (35 cm^3) was stirred. A deep reddish brown solution was formed, followed by precipitation of almost black microcrystals. They were recrystallized from a dmf–thf mixture.

Method 2. A mixture of copper(II) perchlorate hexahydrate (371 mg), bipy (156 mg), and H_2dto (60 mg) (2:2:1 molar ratio) in absolute methanol was stirred under gentle reflux, and microcrystals which separated were recrystallized from a dmf–thf mixture.

Analytical data for the complexes are given in Table 1.

Crystal Structure Analysis of Complex (**2′**).—A dmf solution of the complex was prepared and over this solution cyclohexane was carefully layered. After several days blue prismatic crystals

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Elemental analyses (%) of the complexes

	Found				Calc.			
Complex	C	H	N	Cu	C	H	N	Cu
(1) $[Cu_2(bipy)_2(oxd)][NO_3]_2$	40.60	2.95	17.20	19.80	40.70	2.80	17.25	19.55
(2) $[Cu_2(bipy)_2(oxd)][ClO_4]_2$	36.50	2.60	11.65	17.80	36.50	2.50	11.60	17.55
(2′) $[Cu_2(bipy)_2(oxd)][ClO_4]_2{\cdot}2dmf$	38.45	3.50	12.60		38.65	3.70	12.85	
(3) $[Cu_2(phen)_2(oxd)][NO_3]_2$	44.50	2.80	15.95	17.70	44.75	2.60	16.05	18.20
(4) $[Cu_2(phen)_2(oxd)][ClO_4]_2{\cdot}2dmf$	41.60	3.55	12.25	14.20	41.85	3.50	12.20	13.85
(5) $[Cu_2(bipy)_2(dto)][NO_3]_2$	38.70	2.90	16.30	18.70	38.75	2.65	16.45	18.65
(6) $[Cu_2(bipy)_2(dto)][ClO_4]_2$	34.60	2.50	11.00	16.60	34.95	2.40	11.10	16.80
(7) $[Cu_2(phen)_2(dto)][NO_3]_2$	42.95	2.60	15.25	17.70	42.55	2.45	15.30	17.35

Table 2. Positional parameters (× 10^4) of complex (**2′**) with their e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Cu	−341(2)	1 759(2)	2 267(2)
O(1)	698(12)	349(10)	2 006(13)
N(1)	1 010(10)	−1 187(9)	−95(11)
N(2)	17(11)	2 286(10)	4 563(11)
N(3)	−1 625(11)	2 999(10)	2 482(12)
C(1)	465(14)	−241(12)	500(14)
C(2(	936(15)	1 920(14)	5 497(17)
C(3)	1 149(15)	2 381(14)	7 082(17)
C(4)	370(17)	3 255(15)	7 707(16)
C(5)	−555(14)	3 639(13)	6 777(16)
C(6)	−726(13)	3 142(11)	5 185(14)
C(7)	−1 643(13)	3 518(11)	4 073(14)
C(8)	−2 583(15)	4 327(13)	4 461(16)
C(9)	−3 388(15)	4 622(14)	3 285(18)
C(10)	−3 320(16)	4 109(15)	1 739(20)
C(11)	−2 367(14)	3 307(13)	1 448(19)
Cl	2 866(4)	3 502(3)	1 695(4)
O(2)	3 192(14)	2 751(14)	341(14)
O(3)	3 229(12)	2 997(11)	3 072(13)
O(4)	3 579(11)	4 826(10)	1 797(12)
O(5)	1 446(10)	3 485(9)	1 605(12)
O(D)	2 794(14)	−539(15)	3 879(20)
N(D)	4 815(17)	−688(14)	2 799(22)
C(D1)	6 028(26)	−53(23)	2 184(33)
C(D2)	4 814(26)	−1 988(21)	3 109(33)
C(D3)	3 826(23)	−103(21)	3 164(30)

separated as 2 dmf adduct. The crystals effloresced in the atmosphere, therefore a crystal with dimensions 0.5 × 0.3 × 0.3 mm was sealed in a glass capillary tube and subjected to *X*-ray analysis. Diffraction data were obtained on a Rigaku Denki AFC-5 four-circle diffractometer, using graphite-monochromatized Mo-K_α radiation at 20 °C. Three standard reflections were monitored every 100, and showed a slight decrease in intensity during data collection (*ca.* 6%). The data were rescaled to correct for this.

Crystal data. $C_{11}H_9ClCuN_3O_5{\cdot}C_3H_7NO$, $M = 435.31$, triclinic, space group $P\bar{1}$, $a = 10.079(2)$, $b = 10.457(2)$, $c = 8.556(2)$ Å, $\alpha = 96.49(2)$, $\beta = 91.94(2)$, $\gamma = 100.69(1)°$, $U = 879.1$ Å^3, $D_c = 1.644$ g cm^{-3}, $Z = 2$, $F(000) = 444$, μ(Mo-K_α) = 14.3 cm^{-1}, scan mode θ—2θ, scan width $(1.2 + 0.5 \tan\theta)°$, scan speed 6° min^{-1}, 2θ range 2.5—48°, octant measured $+h, \pm k, \pm l$, unique data with $|F_o| > 3\sigma(|F_o|)$ 2 583, $R = 0.1 033$.

Reflection data were corrected for Lorentz-polarization effects but not for absorption. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method using the UNICS III computer program system[17] on a FACOM M 780 computer at the Computer Center of Kyushu University. Hydrogen atoms were included in their calculated positions and not refined. In the least-squares calculation the function minimized was $\Sigma(|F_o| - |F_c|)^2$ and unit weights were adopted. The final Fourier difference synthesis showed several peaks around copper (1.5 e Å^{-3}). Final positional parameters with their estimated standard deviations (e.s.d.s) are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Other Physical Measurements.—Elemental analyses (C, H, and N) were obtained at the Elemental Analysis Service Center, Kyushu University. Copper analyses were made on a Shimadzu AA-680 atomic absorption/flame emission spectrophotometer. Magnetic susceptibilities were determined in the temperature range 80—300 K using a Faraday balance designed in our laboratory. The apparatus was calibrated by the use of $[Ni(en)_3]$ $[S_2O_3]$ (en = ethylenediamine).[18] Diamagnetic corrections were made using Pascal's constants. Infrared spectra were recorded on a JASCO IR-810 spectrometer on KBr disks or Nujol mulls, electronic spectra on a Shimadzu Multipurpose spectrophotometer model MPS-2000 in dmf. Cyclic voltammograms were determined on an instrument comprised of a HA-501 potentiostat/galvanostat, a HB-104 function generator, and a HF-201 Coulomb/Amperehour meter (Hokuto Denko Ltd.). The measurements were made in dmf solutions containing 10^{-1} mol dm^{-3} tetrabutylammonium perchlorate as the supporting electrolyte, using glassy carbon as the working electrode, a platinum wire as the counter electrode, and a saturated calomel electrode (s.c.e.) as the reference. Controlled-potential electrolyses were made under an argon atmosphere using a platinum net as the working electrode.

Results and Discussion

Preparations.—The oxd-bridged complexes (**1**)—(**4**) were obtained by the reaction of $[Cu(bipy)_2]X_2$ or $[Cu(phen)_2]X_2$ ($X = NO_3$ or ClO_4) with oxamide in methanol in the presence of a base. The use of LiOH as the base gave good results because it and its salts ($LiNO_3$ and $LiClO_4$) formed in the reaction are all fairly soluble in methanol and the products are little contaminated with these inorganic materials. Similarly the dto-bridged complexes (**5**)—(**7**) were obtained by the reaction of $[Cu(bipy)_2]X_2$ or $[Cu(phen)_2]X_2$ with dithio-oxamide, but without use of any base. They could also be obtained by treating stoicheiometric amounts of a copper(II) salt (nitrate or perchlorate), an end-cap ligand (bipy or phen), and dithio-oxamide in methanol. On the other hand, all our attempts to obtain oxd- and dto-bridged complexes with ethylenediamine, diethylenetriamine, or pentane-2,4-dione as the end-cap ligand were in vain.

Indeed bipy and phen seem excellent end-cap ligands to afford oligonuclear copper(II) complexes. This probably relates to a peculiar co-ordination mode of these ligands toward metal ions. That is, when two molecules of bipy or phen (L) co-ordinate to a metal ion such as copper(II), palladium(II), and

Table 3. Bond distances (Å) and angles (°) for [$Cu_2(bipy)_2(oxd)][ClO_4]_2$·2dmf (**2′**)

(*a*) Binuclear cation			
Cu–O(1)	1.959(12)	Cu–N(1′)	1.944(9)
Cu–N(2)	1.981(9)	Cu–N(3)	1.994(11)
Cu–O(5)	2.433(9)	O(1)–C(1)	1.36(2)
N(1)–C(1)	1.28(2)	C(1)–C(1′)	1.44(2)
N(2)–C(2)	1.34(2)	N(2)–C(6)	1.35(2)
C(2)–C(3)	1.38(2)	C(3)–C(4)	1.39(2)
C(4)–C(5)	1.35(2)	C(5)–C(6)	1.40(2)
C(6)–C(7)	1.44(2)	N(3)–C(7)	1.41(2)
C(7)–C(8)	1.41(2)	C(8)–C(9)	1.37(2)
C(9)–C(10)	1.38(2)	C(10)–C(11)	1.40(2)
N(3)–C(11)	1.25(2)		
(*b*) Perchlorate anion			
Cl–O(2)	1.41(1)	Cl–O(3)	1.41(1)
Cl–O(4)	1.43(1)	Cl–O(5)	1.43(1)
(*c*) dmf			
O(D)–C(D3)	1.26(3)	N(D)–C(D3)	1.29(3)
C(D1)–N(D)	1.43(3)	C(D2)–N(D)	1.41(3)
(*a*) Binuclear cation			
O(1)–Cu–N(2)	98.9(4)	O(1)–Cu–N(1′)	86.1(4)
N(2)–Cu–N(3)	83.6(4)	N(3)–Cu–N(1′)	90.2(4)
O(5)–Cu–O(1)	96.2(4)	O(5)–Cu–N(2)	92.9(4)
O(5)–Cu–N(3)	91.0(4)	O(5)–Cu–N(1′)	94.5(4)
Cu–O(1)–C(1)	108(1)	Cu–N(1′)–C(1′)	111(1)
O(1)–C(1)–N(1)	125(1)	O(1)–C(1)–C(1′)	117(1)
C(1)–C(1′)–N(1′)	118(1)	Cu–N(2)–C(2)	127(1)
Cu–N(2)–C(6)	114(1)	C(2)–N(2)–C(6)	119(1)
N(2)–C(2)–C(3)	123(1)	C(2)–C(3)–C(4)	118(1)
C(3)–C(4)–C(5)	120(2)	C(4)–C(5)–C(6)	119(1)
C(5)–C(6)–N(2)	121(1)	C(5)–C(6)–C(7)	124(1)
N(2)–C(6)–C(7)	115(1)	C(6)–C(7)–N(3)	117(1)
C(6)–C(7)–C(8)	125(1)	N(3)–C(7)–C(8)	118(1)
C(7)–C(8)–C(9)	119(1)	C(8)–C(9)–C(10)	121(1)
C(9)–C(10)–C(11)	116(2)	C(10)–C(11)–N(3)	125(2)
C(11)–N(3)–C(7)	121(1)	Cu–N(3)–C(11)	129(1)
Cu–N(3)–C(7)	110(1)		
(*b*) Perchlorate anion			
O(2)–Cl–O(3)	110.9(8)	O(2)–Cl–O(4)	110.8(8)
O(2)–Cl–O(5)	108.6(8)	O(3)–Cl–O(4)	107.3(7)
O(3)–Cl–O(5)	110.1(7)		
(*c*) dmf			
C(D1)–N(D)–C(D2)	115(2)	C(D1)–N(D)–C(D3)	123(2)
C(D2)–N(D)–C(D3)	122(2)	O(D)–C(D3)–N(D)	127(2)

platinum(II) to form planar complexes $[ML_2]^{2+}$ the configuration around the metal is more or less distorted from a rigid square plane because of a significant interligand steric repulsion.[19,20] Because of this, copper(II) complexes of bipy or phen often appear as five- or six-co-ordinate species.[21] Further, one of the bipy or phen ligands is readily replaced with other ligands to afford mixed-ligand complexes.[22] Thus, the reaction of $[Cu(bipy)_2]^{2+}$ or $[Cu(phen)_2]^{2+}$ with ligands capable of acting as bridges leads to the formation of oligonuclear copper(II) complexes, such as dihydroxo-bridged binuclear,[23] imidazolate-bridged cyclic trinuclear,[24] and glyoximate-bridged linear trinuclear[25] complexes. The same steric effect must play a role in the facile formation of the present oxd- and dto-bridged complexes.

Crystal Structure of $[Cu_2(bipy)_2(oxd)][ClO_4]_2$·2dmf (**2′**).—The ORTEP view of the crystal is given in Figure 1, together with the atom numbering system. Bond distances and angles are given in Table 3.

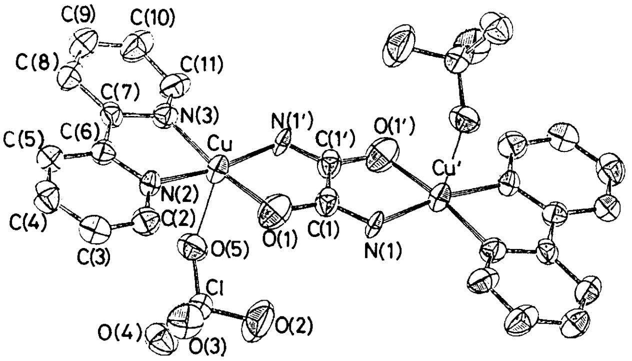

Figure 1. ORTEP view of $[Cu_2(bipy)_2(oxd)][ClO_4]_2$ (**2′**)

The crystal structure is essentially similar to that of $[Cu_2(bipy)_2(oxd)][NO_3]_2$·$3H_2O$ reported previously.[10] The oxamidate ion, which is situated on a crystallographic inversion centre, bridges two copper(II) ions with the Cu···Cu separation of 5.192(2) Å. It is in the *trans* conformation, affording identical co-ordination environments for the two copper(II) ions. The configuration around each copper may be regarded as distorted square pyramid with two nitrogens [N(2) and N(3)] of bipy and one nitrogen [N(1)] and one oxygen [O(1)] of the oxamidate group in the basal plane and with one of the perchlorate oxygens [O(5)] at the apical site. All the equatorial bonds are similar to those of the nitrate salt reported previously,[10] whereas the axial Cu–O(5) (perchlorate) bond distance [2.433(9) Å] is slightly elongated compared with the Cu–O (nitrate) bond distance [2.322(4) Å] of the nitrate salt. The deviation of the copper from the basal plane is small (0.13 Å) and the cation molecule is nearly coplanar. The *X*-ray result also indicates that the dmf molecules are not co-ordinated, but captured in the crystal lattice.

I.R. and Electronic Spectra.—Selected i.r. spectral data are summarized in Table 4. The N–H and C=O vibrations of the bridging oxamidate group appear in the region 3 295—3 290 and at 1 620 cm^{-1}, respectively. The bridging dto is characterized by intense vibrations at ≈1 540 and ≈1 440 cm^{-1}.[26] The N–H vibration for this group appears at 3 255 cm^{-1}. The nitrate vibration appears as split bands at ≈1 395 and ≈1 330 cm^{-1}. Similarly, the perchlorate vibration near 1 100 cm^{-1} splits into two (see Table 4). These facts are indicative of the co-ordination of the anions as unidentate ligands, in accord with the present *X*-ray result for $[Cu_2(bipy)_2(oxd)][ClO_4]_2$·2dmf and the previous result for $[Cu_2(bipy)_2(oxd)][NO_3]_2$·$3H_2O$.[10] For (**2′**) and (**4**) an i.r. band attributable to ν(C=O) of the lattice dmf molecules is found at 1 650 cm^{-1}.

The electronic spectra of the complexes were measured in dmf and on powder samples. The numerical data are summarized in Table 4.

When measured on powder samples the oxd-bridged complexes (**1**)—(**4**) each showed a *d–d* band around 17 000 cm^{-1}. The complexes were tolerably soluble in dmf (up to 5×10^{-4} mol dm^{-3} per copper) and in this solvent the *d–d* band maximum was located at (16.0—16.4) × 10^3 cm^{-1}. The solution spectra were studied in the concentration range 1×10^{-5}—5×10^{-4} mol dm^{-3} (per copper ion) and it was found that the spectra in the u.v. and near-u.v. regions changed on dilution, though the frequency and the absorption coefficient of the *d–d* band were little influenced on dilution. Thus, the complexes are more or less decomposed at 5×10^{-4} mol dm^{-3}.

The dto-bridged complexes (**5**)—(**7**) are considerably soluble in dmf. Their electronic spectra essentially obey Beer's law at concentrations higher than 5×10^{-4} mol dm^{-3} and show an

Table 4. Selected i.r. and electronic spectral data

	I.r. (cm^{-1})					Electronic absorption*
Complex	N-H	oxd^{2-}	dto^{2-}	NO_3^-	ClO_4^-	ν/cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})
(1)	3 290	1 620		1 400 1 330		16 390 (130)
(2)	3 295	1 620			1 110 1 090	16 000 (95)
(3)	3 290	1 620		1 395 1 335		16 260 (120)
(4)	3 295	1 620			1 110 1 090	16 310 (105)
(5)	3 250		1 543 1 450	1 393 1 330		15 870 (sh) (920) 21 740 (2 020)
(6)	3 260		1 538 1 440		1 100 1 070	16 130 (sh) (890) 21 900 (1 880)
(7)	3 250		1 535 1 430	1 395 1 320		15 630 (sh) (725) 21 640 (1 760)

* Determined in dmf at $\approx 5 \times 10^{-4}$ mol dm^{-3} (per copper) for complexes **(1)**—**(4)** and at $\approx 1 \times 10^{-3}$ mol dm^{-3} for **(5)**—**(7)**; ε for one copper atom; sh = shoulder.

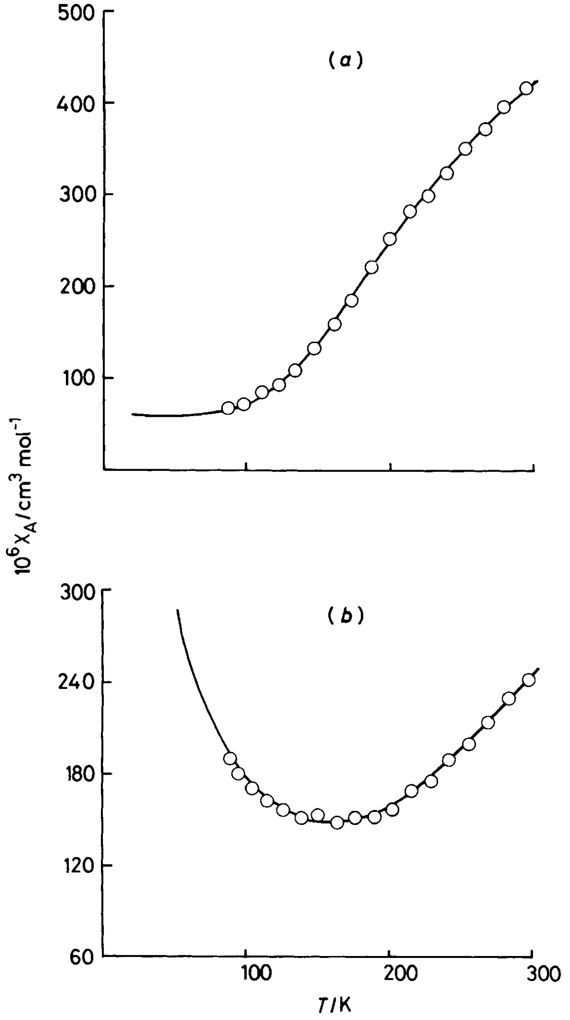

Figure 2. Temperature variations of the magnetic susceptibility of complexes **(1)** (*a*) and **(5)** (*b*). The solid curves are based on equation (1) and the magnetic parameters in Table 5

Table 5. Magnetic parameters of the complexes

Complex	μ/μ_B*	$-J/cm^{-1}$	g	10^6 $N\alpha/cm^3$ mol^{-1}	p
(1)	0.99	254	2.03	60	0
(2)	0.99	277	2.14	50	0.024
(3)	1.06	244	2.11	50	0.035
(4)	0.98	283	2.20	60	0.006
(5)	0.76	363	2.05	60	0.030
(6)	0.80	434	2.05	60	0.055
(7)	0.61	491	2.13	50	0.028

* Moment (per copper atom) at room temperature.

intense band around 22 000 cm^{-1}. This band is also seen in reflectance spectra and may be assigned to a charge-transfer (c.t.) band from the sulphur of dithio-oxamidate ion to the copper(II) ion.[14] The *d–d* band is superposed on the c.t. band and barely observed as a discernible shoulder. At concentrations lower than 5×10^{-4} mol dm^{-3} Beer's law did not hold and the intensity of the c.t. band was diminished on dilution.

Magnetic Properties.—Room-temperature magnetic moments (per copper atom) for the oxd-bridged complexes fall in the range 0.98—1.06 μ_B. Those for the dto-bridged complexes are substantially lower (0.61—0.80 μ_B). The operation of an antiferromagnetic spin exchange within each complex molecule is probably the reason for the reduced magnetic moments.

The temperature variations of the magnetic susceptibility were determined in the range 80—300 K and typical examples are given in Figure 2. In the case of complex **(1)** the susceptibility gradually decreased with temperature and reached a plateau at 80 K [see Figure 2(*a*)]. In the case of **(5)** the magnetic susceptibility also decreased with temperature but increased again below 160 K [see Figure 2(*b*)]. The magnetic behaviour found for the latter complex is characteristic of the presence of a small amount of a monomeric copper(II) species as a paramagnetic impurity. Thus, magnetic simulations were carried out by the Bleaney–Bowers equation[27] (1) involving a correction term for the paramagnetic impurity. In this equation

$$\chi_A = (Ng^2\beta^2/kT)[1/\{3 + \exp(-2J/kT)\}](1 - p) + N\alpha + 0.45p/T \quad (1)$$

p is the mole fraction of the paramagnetic impurity, J the exchange integral, N is Avogadro's number, g the Lande g factor, β the Bohr magneton, T the absolute temperature, and

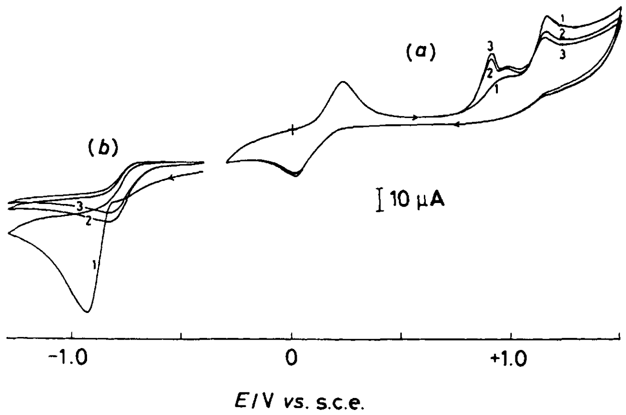

Figure 3. Cyclic voltammograms of complex (**5**): (*a*) sweep in the range −0.3 to +1.5 V and (*b*) sweep in the range −0.4 to −1.3 V. Scan speed 10 mV s^{-1}; *ca.* 1×10^{-3} mol dm^{-3} in dmf; supporting electrolyte 1×10^{-1} mol dm^{-3} NBu_4ClO_4; glassy carbon electrode. The numbers indicate the sweep repetition

$N\alpha$ the temperature-independent paramagnetism. As shown by the solid curves in Figure 2, good magnetic simulations were attained with equation (1). The magnetic parameters thus determined are summarized in Table 5..

The singlet–triplet energy separations ($-2J$) of the oxd-bridged complexes fall in the range 488—566 cm^{-1}. Comparable values have been reported for related oxd-bridged binuclear copper(II) complexes.[12] The $-2J$ values found for the dto-bridged complexes are much larger (726—982 cm^{-1}). Oxalato-(ox)-bridged copper(II) complexes $[Cu_2(bipy)_2(ox)][NO_3]_2$[6] and $[Cu_2(phen)_2(ox)][NO_3]_2$[12] have a structure essentially similar to that of (**2'**) and their $-2J$ values were reported as 385.9 and 330 cm^{-1}, respectively. Thus, it may be concluded that antiferromagnetic superexchange in binuclear copper(II) complexes increases in the order of the bridging group: ox < oxd < dto.

Electrochemistry.—Cyclic voltammograms of the complexes were measured in dmf in order to examine the redox properties. Those of the oxd-bridged complexes (**1**)—(**4**) were very complicated and hardly analysed, probably because the complexes partly decomposed in this solvent as demonstrated by electronic spectral investigations.

On the other hand the dto-bridged complexes (**5**)—(**7**) each showed a simplified cyclic voltammogram. In Figure 3 is given the cyclic voltammogram of (**5**), which shows one irreversible couple at a potential very close to zero ($E_{pa} = +0.23$ V and $E_{pc} = +0.02$ V *vs.* s.c.e.). This couple showed a good reversibility to repetitive sweeps (see Figure 3). Similarly, complexes (**6**) and (**7**) showed an irreversible couple at nearly the same potential $E_{pa} = +0.21$ and $+0.24$, $E_{pc} = +0.01$ and -0.02 V, respectively. Besides this couple two irreversible waves are seen at a more positive potential (+1.1 V) and at a negative potential (−0.9 V) (see Figure 3). These waves changed with repetitive sweeps. Thus, our attention was focussed on the couple near +0.1 V.

Coulometric experiments at +0.2 V indicated an electric current equivalent to the transfer of one electron. In the course of this electrolysis, however, an almost black material (probably a polymeric copper complex of dto) precipitated and this precluded electronic and e.s.r. spectral investigations to characterize the one-electron-reduced species. We tentatively assign this couple to the redox process $Cu^{II}_2 \longrightarrow Cu^{I}Cu^{II}$. Very facile reduction of the dto complexes must be associated with (*i*) the co-ordination of bipy or phen and the sulphur of dithio-oxamidate which provide low-lying vacant orbitals for back donation and (*ii*) the dipositive form of the complexes. For the related dinegative complex $[Cu_2L]^{2-}$ of a dithio-oxamide derivative possessing peptide residues attached to the nitrogens, $C_2S_2(NHCH_2CONHCH_2CONHCH_2CH_2OH)_2$ (H_6L), the step wise oxidations at the metal centre occurred at +0.42 and +0.85 V *vs.* s.c.e. but no reduction wave appeared at the available potentials.[15]

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