A Bridge-bond Isomerism. X-Ray Crystal Structure, Spectral and Magnetic Properties of Two Dinuclear Isomeric Complexes [Cu(bipyo)Cl_2] (bipyo = 2,2′-bipyridine *N,N*′-dioxide)†

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Copper(II) chloride reacts with 2,2′-bipyridine *N,N*′-dioxide (bipyo), in methanolic solution, in a manner depending on the reaction conditions (temperature, ligand : metal ion ratio, concentration, *etc.*) to form different products. Two of them, a green and a yellow-orange isomer of [Cu_2(bipyo)$_2Cl_4$], have been characterized by elemental microanalysis, electronic, IR and ESR spectra and magnetic susceptibility measurements. The crystal and molecular structures of both isomers have been determined from X-ray diffractometer data by the heavy-atom method and refined by full-matrix least-squares. The structures of the green and yellow-orange isomers, respectively, have been refined to $R = 0.054$ (for 1366 reflections) and 0.063 (for 1283 reflections): green isomer, triclinic, space group $P\bar{1}$, $a = 8.664(2)$, $b = 8.732(2)$, $c = 9.099(3)$ Å, $\alpha = 95.62(2)$, $\beta = 107.04(2)$, $\gamma = 114.05(2)°$, and $Z = 1$; yellow-orange isomer, monoclinic, space group $P2_1/c$, $a = 7.912(2)$, $b = 9.878(2)$, $c = 15.086(3)$ Å, $\beta = 99.86(2)°$ and $Z = 2$. Both crystal structures comprise centrosymmetric dimeric [Cu_2(bipyo)$_2Cl_4$] molecules. The copper(II) atoms of the green isomer are bridged by two chlorine atoms, those of the orange-yellow isomer by the oxygen atoms of two bipyo ligands.

Considerable attention has been given to the donor properties of aromatic *N*-oxides.[1] Two basic classes of copper(II) complexes have been prepared and characterized: (*a*) those having the *N*-oxide ligands as bridges, which usually result in low magnetic moments; and (*b*) those containing non-bridging *N*-oxide ligands, which exhibit normal magnetic moments. 2,2′-Bipyridine *N,N*′-dioxide (bipyo) has a further possibility as a chelating ligand. However, despite this, significantly less work has been done in the preparation and structural characterization of the copper complexes with bipyo.[2–5]

As a part of our interest in chelating ligands which stabilize the copper(II) oxidation state, we have studied the bipyo complexes of copper(II) salts. Two different isomeric complexes of composition Cu(bipyo)Cl_2 have been obtained. Since the green and the yellow-orange isomers differ significantly in their magnetic and other properties we decided to solve their structures. The results of the X-ray structure determination together with their syntheses, spectroscopic characterization and magnetic properties are presented in this paper. A brief preliminary report of the preparation and some properties has appeared.[6]

Results and Discussion

Structures of [Cu_2(bipyo)$_2Cl_4$].—The crystal structures of both isomers consist of dimeric molecules [Cu_2(bipyo)$_2Cl_4$] **1** held together by van der Waals interactions and weak hydrogen bonds. Only half of the dimeric molecules are crystallographically unique in both isomers. The final fractional positional coordinates of the non-hydrogen atoms of both isomers are listed in Table 1.

The structure of the green isomer of **1** and the atom numbering are shown in Fig. 1 while the relevant interatomic distances and bond angles are presented in Table 2. The dimeric molecule is centrosymmetric with the symmetry centre between atoms Cu and Cu′. Two chlorine atoms [Cl(1) and Cl(2)] and two oxygen atoms [O(1) and O(2)] of the bipyo ligand are bonded to the copper atom in the independent part of **1** thus forming the distorted square base of a nearly square-pyramidal co-ordination. The co-ordination is completed by the chlorine atom Cl(2′) of the symmetrically dependent part of **1** thus forming two square-pyramidal polyhedrons connected *via* the common body edge. The Cu–Cl and Cu–O bond distances [2.265(1), 2.278(1) and 1.964(3), 2.014(3) Å, respectively] are within the range typical for the basal plane of a square pyramid, while the apical Cl(2′) atom is at a distance typical for this position [2.626(1) Å]. The copper atom is displaced from the basal plane of the donor atoms by 0.270(1) Å and the apical Cl(2′) atom is slightly moved (0.31 Å) from the regular axial

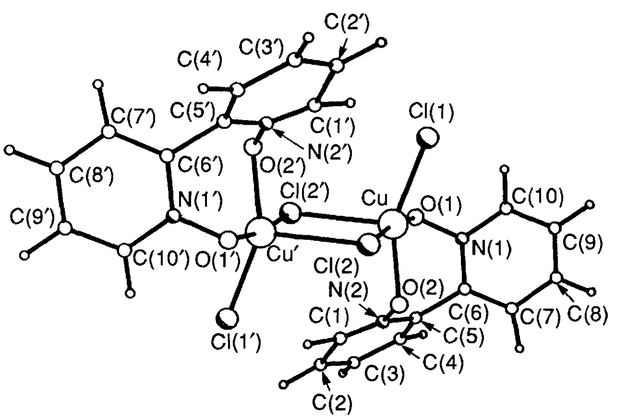

Fig. 1 Molecular structure and atomic numbering of the green isomer of [Cu_2(bipyo)$_2Cl_4$]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI units employed: Oe = 10^3 A m^{-1}, G = 10^{-4} T.

Table 1 Final positional parameters (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses

	(*a*) Green isomer			(*b*) Yellow-orange isomer		
Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	2206(1)	1466(1)	1055(1)	658(1)	1307(1)	4450(1)
Cl(1)	2246(1)	3088(1)	3178(1)	3076(2)	2469(1)	4824(1)
Cl(2)	487(1)	−1126(1)	1444(1)	−1014(2)	2783(1)	3603(1)
O(1)	3882(4)	3567(3)	665(3)	−1303(4)	−6(3)	4480(2)
O(2)	3254(4)	293(3)	−88(3)	1349(4)	−102(3)	3467(2)
N(1)	5618(4)	3922(4)	1313(4)	−2316(5)	−353(4)	3703(2)
N(2)	3593(4)	760(4)	−1335(4)	1326(5)	−1409(4)	3672(3)
C(1)	2377(6)	−202(6)	−2767(5)	−3835(6)	265(5)	3479(4)
C(2)	2764(7)	167(7)	−4129(5)	−4920(7)	−97(6)	2710(4)
C(3)	4359(8)	1488(7)	−3944(6)	−4429(8)	−1076(6)	2167(4)
C(4)	5567(6)	2527(6)	−2450(5)	−2862(6)	−1710(6)	2412(4)
C(5)	5186(5)	2158(5)	−1142(5)	−1797(7)	−1356(5)	3188(3)
C(6)	6369(6)	3253(5)	470(5)	−186(6)	−2083(5)	3534(3)
C(7)	8191(6)	3745(6)	1088(6)	−211(7)	−3485(5)	3671(4)
C(8)	9261(6)	4898(6)	2568(6)	1275(8)	−4154(5)	4002(4)
C(9)	8470(6)	5473(6)	3440(5)	2796(8)	−3425(6)	4178(4)
C(10)	6606(6)	4954(5)	2783(5)	2791(6)	−2057(6)	4009(4)

Table 2 Interatomic distances (Å) and angles (°) with e.s.d.s in parentheses

(*a*) Green isomer

Cu–Cl(1)	2.265(1)	Cl(1)–Cu–Cl(2)	95.1(1)
Cu–Cl(2)	2.278(1)	Cl(1)–Cu–O(1)	90.2(1)
Cu–O(1)	1.964(3)	Cl(1)–Cu–O(2)	154.1(1)
Cu–O(2)	2.014(3)	Cl(1)–Cu–Cl(2′)	107.9(1)
Cu–Cl(2′)	2.626(1)	Cl(2)–Cu–O(1)	172.6(1)
Cu • • • Cu′	3.409(1)	Cl(2)–Cu–O(2)	89.1(1)
O(1)–N(1)	1.331(4)	Cl(2)–Cu–Cl(2′)	92.2(1)
O(2)–N(2)	1.315(5)	O(1)–Cu–O(2)	83.9(1)
N(2)–C(1)	1.332(5)	O(1)–Cu–Cl(2′)	90.9(1)
N(2)–C(5)	1.367(6)	O(2)–Cu–Cl(2′)	97.4(1)
N(1)–C(6)	1.367(5)	Cu–O(1)–N(1)	113.6(2)
N(1)–C(10)	1.341(5)	Cu–O(2)–N(2)	119.9(2)
C(1)–C(2)	1.409(7)	Cu–O(1)–Cu′	109.2(1)
C(2)–C(3)	1.340(9)	O(2)–N(2)–C(1)	118.0(3)
C(3)–C(4)	1.385(7)	O(2)–N(2)–C(5)	120.1(3)
C(4)–C(5)	1.359(7)	O(1)–N(1)–C(6)	119.8(3)
C(5)–C(6)	1.470(7)	O(1)–N(1)–C(10)	119.0(3)
C(6)–C(7)	1.368(7)		
C(7)–C(8)	1.389(6)		
C(8)–C(9)	1.369(7)		
C(9)–C(10)	1.399(6)		

(*b*) Yellow-orange isomer

Cu–Cl(1)	2.219(1)	Cl(1)–Cu–Cl(2)	102.2(1)
Cu–Cl(2)	2.221(1)	Cl(1)–Cu–O(1)	162.5(1)
Cu–O(1)	2.028(3)	Cl(1)–Cu–O(2)	101.5(1)
Cu–O(2)	2.173(4)	Cl(1)–Cu–O(1′)	92.1(1)
Cu–O(1′)	2.061(3)	Cl(2)–Cu–O(1)	92.9(1)
Cu • • • Cu′	3.333(1)	Cl(2)–Cu–O(2)	102.7(1)
O(1)–N(1)	1.349(6)	Cl(2)–Cu–O(1′)	154.7(1)
O(2)–N(2)	1.328(6)	O(1)–Cu–O(2)	83.6(1)
N(1)–C(1)	1.339(8)	O(1)–Cu–O(1′)	70.8(1)
N(1)–C(5)	1.366(8)	O(2)–Cu–O(1′)	89.1(1)
N(2)–C(6)	1.354(7)	Cu–Cl(2)–Cu′	87.8(1)
N(2)–C(10)	1.346(8)	Cu–O(1)–N(1)	119.1(1)
C(1)–C(2)	1.369(9)	Cu–O(2)–N(2)	116.6(3)
C(2)–C(3)	1.367(10)	O(1)–N(1)–C(1)	118.6(5)
C(3)–C(4)	1.382(9)	O(1)–N(1)–C(5)	119.2(5)
C(4)–C(5)	1.368(9)	O(2)–N(2)–C(6)	119.3(5)
C(5)–C(6)	1.479(8)	O(2)–N(2)–C(10)	120.3(5)
C(6)–C(7)	1.400(8)		
C(7)–C(8)	1.367(9)		
C(8)–C(9)	1.388(10)		
C(9)–C(10)	1.367(9)		

position [see also Table 2 for the angles including the Cu–Cl(2′) bond].

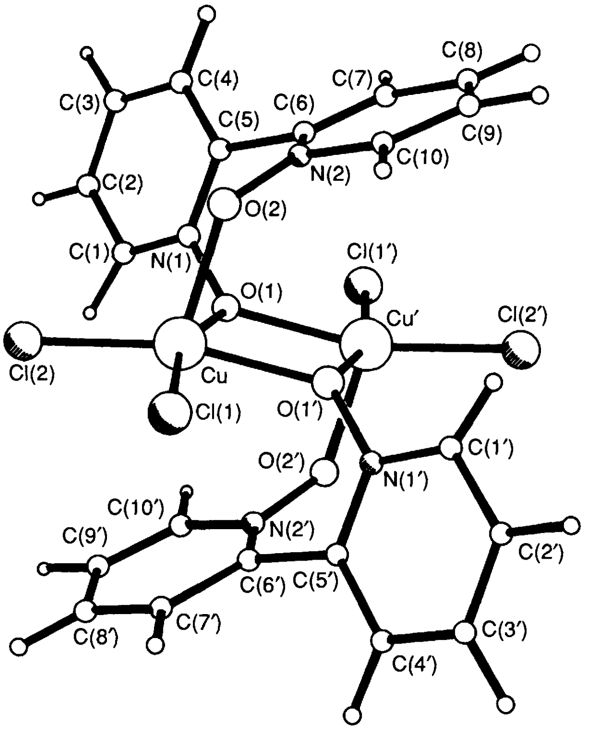

Fig. 2 Molecular structure and atomic numbering of the yellow-orange isomer of [$Cu_2(bipyo)_2Cl_4$]

The structure of the yellow-orange isomer of compound **1** and the numbering scheme are presented in Fig. 2. Selected bond distances and angles are shown in Table 2. The centrosymmetric molecule has the symmetry centre between the Cu and Cu′ atoms. Besides two chlorine atoms [Cl(1) and Cl(2)] and two oxygen atoms of the bipyo molecule [O(1) and O(2)] of the independent part of **1**, the co-ordination polyhedron of the Cu atom is completed by the bridging atom O(1′) of a centrosymmetrically related bipyo molecule. The Cl(1), Cl(2), O(1) and O(1′) atoms form a rather distorted square base of a square-pyramidal polyhedron; thus two polyhedrons share a basal edge. The basal Cu–Cl(1), Cu–Cl(2), Cu–O(1) and Cu–O(1′) distances are 2.219(1), 2.221(1), 2.028(3) and 2.061(3) Å, respectively. The apical Cu–O(2) distance [2.173(4) Å] is greater than the other two Cu–O distances, but the differences are unexpectedly small. The Cu atom is displaced above the basal plane of the donor atoms by 0.244(1) Å, and the apical

O(2) atom is shifted from its regular position by 0.527 Å [see also Table 2 for the angles involving the Cu–O(2) bond].

According to the data the square pyramid of the Cu atom in the yellow-orange isomer seems to be more distorted than in the green isomer. In spite of this the parameter proposed for distinguishing between tetragonal-pyramidal and trigonal-bipyramidal co-ordination geometries[7] has a smaller value (τ = 13.0%) for the yellow-orange than for the green isomer (τ = 30.8%). However, in both cases the values are closer to the value for a pure tetragonal-pyramidal geometry (τ = 0%). Thus the greater distortion of the yellow-orange isomer cannot be explained by the deformation leading to the trigonal-bipyramidal polyhedron, rather as a consequence of the bridging mode of the bipyo ligand.

The other difference between the two isomers is in their chromophores, $CuCl_3O_2$ for the green isomer and $CuCl_2O_3$ for the yellow-orange isomer, arising from the different bridging ligands. This difference raises the question of the classification of the isomerism. Generally speaking these isomers differ one from another in the bonding mode of the ligands and from this point of view could be classified as bonding isomers. However, there is a significant difference between this pair of isomers and others; bond isomerism is known for ligands able to bond *via* different atoms. In this case the same atoms of the ligands (two oxygen atoms of bipyo and two Cl atoms per copper atom) are used for bond formation, but the modes of bonding are different. The main difference between these two isomers is in the atoms which form the bridges between two copper atoms (Cl in the green isomer and O in the yellow-orange one), while other characteristics (co-ordination polyhedron, chelation, mode of bipyo, *etc.*) are the same. Thus the term bridge-bond isomerism is suggested.

Moreover, the present structures and properties can be compared with those of copper complexes with other aromatic *N*-oxides. A few pairs of isomers[8–11] show the stoichiometry $[Cu(N\text{-oxide})_2Cl_2]$ (*N*-oxide = pyridine *N*-oxide, 4-methyl-, 3-methyl-, 2,6-dimethyl- or 2,4,6-trimethyl-pyridine *N*-oxide) but the structures have been solved[12,13] only for the 4-methylpyridine *N*-oxide pair. The green isomer is monomeric with a nearly planar co-ordination polyhedron and the yellow isomer has a dimeric structure $[\{CuL_2Cl_2\}_2]$ with bridging *N*-oxide (L) ligands and this complex is partly suitable for comparison with the yellow-orange isomer of **1**. The structures of some dimeric complexes of general formula $[\{Cu(pyo)LCl_2\}_2]$ [pyo = pyridine *N*-oxide; L = pyo,[14] H_2O,[15–17] or dimethyl sulphoxide (dmso)[18]] are more suitable for structural comparison because they contain pyo bridging ligands and the apical positions are occupied by oxygen-donor ligands. It is interesting that the Cu–O(apical) distance [2.187(1) Å] for L = pyo[14] is very close to that found in the yellow-orange isomer of **1** [see Table 2 for the Cu–O(2) distance]. The unexpectedly short Cu–O(apical) distances in both these complexes seem to be caused by the nature of the ligands because for the other oxygen-donor apical ligands this distance is slightly longer [2.336(3), 2.342(4), 2.266(4) and 2.279(6) Å for L = H_2O,[15] H_2O,[16] H_2O[17] and dmso,[18] respectively]. All other structural parameters (*e.g.* copper–basal plane distance, mutual orientation of pyridine *N*-oxide ring and basal plane, *etc.*) are very close to each other for all complexes compared.

No structure of an aromatic *N*-oxide–copper(II) halide complex is known which could be compared with the dimeric structure of the green isomer of **1**. There are known[19,20] only some polymeric complexes of stoichiometry $[\{Cu(pyo)Cl_2\}_n]$ or $[\{Cu_3L_2Cl_6(H_2O)_2\}_n]$ (L = 2-methylpyridine *N*-oxide) which contain alternate chloride and *N*-oxide bridges. The copper(II) atoms in those complexes show a wider variety of co-ordination polyhedrons.[1]

Table 3 ESR spectroscopic splitting factors[a] of the green isomer of $[Cu_2(bipyo)_2Cl_4]$

T/K	g_x	g_y	g_z	g_{av}[b]
293	2.04_7	2.07_5	2.32_2	2.15_2
77	2.04_5	2.07_6	2.32_6	2.15_3
4.2	2.04_0	2.07_5	2.32_2	2.14_9

[a] No monomeric form of the complex was observed. [b] $g_{av}^2 = (g_x^2 + g_y^2 + g_z^2)/3$.

Table 4 Magnetic data[a] for the green isomer of $[Cu_2(bipyo)_2Cl_4]$

T/K	$10^6\chi_{Cu}$[b]/cm³ mol⁻¹	μ_{eff}[c]
4.2	59 400	1.41
10	29 300	1.53
25	15 000	1.73
50	8 200	1.81
100	4 170	1.83
150	2 800	1.83
200	2 110	1.84
250	1 710	1.85
290	1 480	1.85

[a] Data selected from 66 experimental points. [b] $\chi_{Cu} = M\chi^{corr}/2$, where M = molecular weight; $\chi(SI) = (4\pi \times 10^6)\chi(cgs)$. [c] $\mu_{eff} = 2.83(\chi_{Cu}T)^{\frac{1}{2}}$.

Table 5 Magnetic parameters of the green isomer of $[Cu_2(bipyo)_2Cl_4]$

T/K	Curie constant, C/cm³ K mol⁻¹	Weiss constant, θ/K
4.2–25	0.413	−3.8
50–290	0.433	−3.8
4.2–290	0.433	−4.1

Table 6 Magnetic data for the yellow-orange isomer of $[Cu_2(bipyo)_2Cl_4]$

T/K	$10^6\chi_{Cu}$/cm³ mol⁻¹	μ_{eff}
174	4	0.07
183	11	0.13
195	24	0.19
205	30	0.22
214	36	0.25
222	46	0.29
232	68	0.35
242	78	0.39
251	99	0.45
261	108	0.47
271	133	0.54
281	147	0.57
298	181	0.66

Magnetic Susceptibility and ESR Spectra of $[Cu_2(bipyo)_2Cl_4]$.—Variable-temperature magnetic susceptibility measurements and ESR spectra of complex **1** revealed great differences in the magnetic properties of the two isomers.

The ESR spectrum of the green isomer was measured at three temperatures, *e.g.* room, 77 K and liquid-helium temperature. The spectrum shows a rhombic signal with two features in the perpendicular region (g_y = 2.07 and g_x = 2.04) and one in the parallel region (g_z = 2.32). It does not change with temperature (Table 3). The spectrum is consistent with the square-pyramidal co-ordination sphere of the copper(II) magnetic centre, and the single unpaired electron is located in an essentially $d_{x^2-y^2}$ orbital. In the region between the signal components corresponding to g_z and g_y an incomplete copper hyperfine pattern has been observed (five lines only). The average interline spacing was *ca.* 44 Oe. This pattern is a clear indication of the presence of a very weak magnetic interaction between the copper centres in the dimeric unit.

The magnetic properties of the green isomer over the

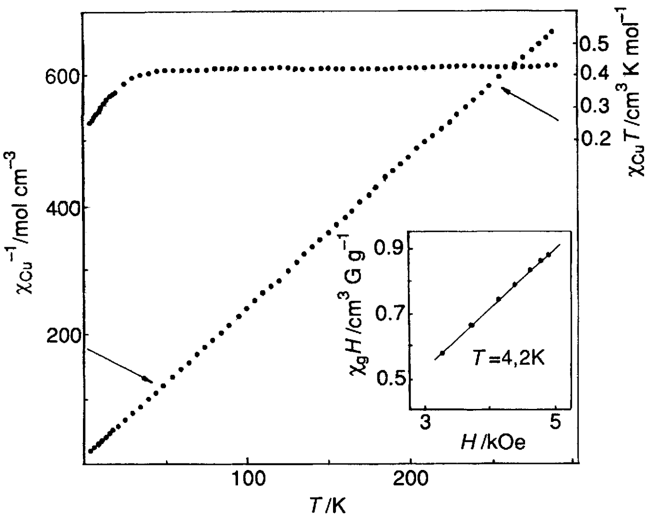

Fig. 3 Variation of the reciprocal molar susceptibility and $\chi_{Cu}T$ with temperature and variation of $\chi_g H$ with H for the green isomer of $[Cu_2(bipyo)_2Cl_4]$

temperature range 4.2–290 K are given in Table 4 and plotted in Fig. 3, while the Curie and Weiss constants are listed in Table 5. The course of the $\chi_{Cu}T$ *vs.* T plot was in accord with the ESR spectra, namely the observed antiferromagnetic interactions are very weak. At higher temperatures the $\chi_{Cu}T$ product was practically constant (about 0.425 cm^3 K mol^{-1}) and decreased only at the lowest temperatures (below 30 K), to 0.249 cm^3 K mol^{-1} at 4.2 K. In such situations the parameter J can be determined only by means of the magnetization equation.[21] The application of the Bleaney–Bowers susceptibility expression would be inappropriate because $J \approx g\beta H$. The Hamiltonian is given by equation (1) where $\hat{S}$ is the total spin operator ($\hat{S} = \hat{S}_A + \hat{S}_B$) and J expresses the intramolecular exchange interaction between spins. The magnetic susceptibility χ_{Cu} is expressed by equation (2) and is corrected, in the molecular field approximation, for the presence of magnetic interaction with neighbouring dimers[22] [equation (3)] where z is the number of nearest-neighbour dimers and J' is the lattice interaction parameter. All other symbols have their usual meanings. The best fit to the data yielded $J = -0.8$ cm^{-1}, $zJ' = -2.9$ cm^{-1} and the agreement factor $R = 3.39 \times 10^{-3}$.

$$\hat{H}_{ex} = -2J(\hat{S}_A \cdot \hat{S}_B) + g\beta H\hat{S} \qquad (1)$$

$$\chi_{Cu} = \frac{Ng\beta \sinh(g\beta H/kT)}{H[\exp(-2J/kT) + 2\cosh(g\beta H/kT) + 1]} + N_\alpha \qquad (2)$$

$$\chi'_{Cu} = \frac{\chi_{Cu}}{1 - (4zJ'\chi_{Cu}/Ng^2\beta^2)} \qquad (3)$$

The ESR spectrum of the yellow-orange isomer of compound **1** at room temperature gives a broad single line of $\delta H_{pp} \approx 500$ Oe for $\nu = 9.385$ GHz. The spectroscopic splitting factor for the centre of the line was 2.11. The sample was free from monomeric impurities.

The magnetic susceptibility data for this isomer are presented in Table 6. The low values of the magnetic susceptibility and of the magnetic moment at temperatures close to room temperature (Table 6) suggest strong antiferromagnetic coupling of the magnetic centres in the complex. This was confirmed by the drastic decrease in both values at decreasing temperature, to zero below 170 K. The magnetic susceptibility of two interacting copper(II) ions can be calculated using the isotropic Heisenberg–Dirac–Van Vleck model[23] resulting in equation (4) where $2J$ is the singlet–triplet energy gap defined by the phenomenological Hamiltonian $\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2$, where J expresses the intramolecular exchange interaction and $\hat{S}_1$ and $\hat{S}_2$ are quantum spin operators. The least-squares best fit of the data yielded $2J = 730$ cm^{-1}, with $R = 3.34 \times 10^{-9}$.

$$\chi_{Cu} = \frac{Ng^2\beta^2}{3kT}\left[1 + \frac{1}{3}\exp(-2J/kT)\right]^{-1} + N_\alpha \qquad (4)$$

Infrared Spectra of $[Cu_2(bipyo)_2Cl_4]$.—The Nujol (mull) and KBr (pellet) IR spectra of compound **1** in the region 400–1700 cm^{-1} are rather complicated, due to the presence of the bipyridine moiety, with many absorptions most of which are not sensitive to the co-ordination mode. Two absorptions at 1220 and 1204 cm^{-1} for the yellow-orange isomer and at 1218 and 1196 cm^{-1} for the green isomer could be assigned to the N–O stretching vibrations and owing to co-ordination they are significantly shifted from their positions for the free ligand[24] (1260 and 1253 cm^{-1}). Smaller shifts were found for the absorptions assignable to the N–O bending vibrations (844 and 833 cm^{-1} for the yellow-orange isomer, 846 and 828 cm^{-1} for the green isomer, 849 and 837 cm^{-1} for the free ligand[24]). Absorptions at 409 cm^{-1} for the yellow-orange isomer and 401 cm^{-1} for the green isomer may be assigned to the Cu–O vibrations and they are close to those ones found for the other *N*-oxide complexes (*e.g.* 388 cm^{-1} for $[\{Cu(pyo)_2Cl_2\}_2]$,[25] 425 cm^{-1} for $[\{Cu(pyo)Cl_2(H_2O)\}_2]$,[25] and 411 cm^{-1} for $[\{Cu(pyo)Cl_2(dmso)\}_2]$[25]). Absorptions assignable to the Cu–Cl vibrations were found at 321 and 310 cm^{-1} for the yellow-orange isomer and at 362, 285, 280 and 249 cm^{-1} for the green isomer. The complex $[\{Cu(pyo)_2Cl_2\}_2]$ exhibits those bands at 316 and 297 cm^{-1}, $[\{Cu(pyo)Cl_2(H_2O)\}_2]$ at 314 cm^{-1} and $[\{Cu(pyo)Cl_2(dmso)\}_2]$[25] at 313 and 274 cm^{-1}.[25]

Electronic Spectra of $[Cu_2(bipyo)_2Cl_4]$.—The reflectance spectra of the solid complex in the region 200–2500 nm shows d–d bands (broad band at 870 nm with unresolved shoulder on the low-energy side for the yellow-orange isomer, and broad band at 815 nm with significant shoulder at 1000 nm for the green isomer), charge-transfer bands (at 430 nm with shoulders at 410 and 392 nm for the yellow-orange complex, and two shoulders at 460 and 378 nm for the green isomer) and bands assignable to intraligand transitions or charge-transfer bands in the UV region (at 332 and 280 nm for the yellow-orange isomer, and at 348 and 280 nm for the green isomer). In this region the free ligand exhibits bands at 348 and 258 nm with a shoulder at 268 nm.

Experimental

Chemicals.—2,2′-Bipyridine and copper(II) chloride dihydrate were of analytical grade (Lachema). Other chemicals were of reagent grade (Lachema) and all were used as received. All solvents were purified and/or dried by standard methods.

Preparations.—2,2′-Bipyridine *N,N′*-dioxide was prepared by 2,2′-bipyridine oxidation with hydrogen peroxide in glacial acetic acid.[2] A mixture of 2,2′-bipyridine (10 g) and hydrogen peroxide (13 cm^3) in glacial acetic acid (75 cm^3) was heated for 3 h at 80 °C. Then another portion of hydrogen peroxide (9 cm^3) was added and the mixture heated for 19 h at 80 °C. The mixture was then cooled and acetone (1 dm^3) added to crystallize the product. The crude product was recrystallized from water by adding acetone. Yield *ca.* 75% (Found: C, 64.60; H, 4.25; N, 14.60. Calc. for $C_{10}H_8N_2O_2$: C, 63.85; H, 4.30; N, 14.90%).

$[Cu_2(bipyo)_2Cl_4]$. *Green isomer.* A solution of $CuCl_2{\cdot}2H_2O$ (10 mmol, 1.70 g) in dry methanol (5 cm^3) was added to a hot solution of bipyo (10 mmol, 1.88 g) in dry methanol (95 cm^3). The clear green solution was allowed to cool and to crystallize. The green product was filtered off, washed with small portions of hot dry methanol and dried *in vacuo*. Yield *ca.* 80% (Found: C, 36.95; H, 2.45; Cu, 19.65; N, 8.55. Calc. for $C_{20}H_{16}Cl_4Cu_2N_4O_4$: C, 37.25; H, 2.50; Cu, 19.70; N, 8.70%). Crystals suitable for X-ray analysis were obtained by slow crystallization from methanol–dioxane (1:2 v/v).

Yellow-orange isomer. A solution of bipyo (20 mmol, 3.76 g) in methanol (350 cm^3) was added to a solution of $CuCl_2 \cdot 2H_2O$ (20 mmol, 3.41 g) in methanol (30 cm^3). The clear green solution was then refluxed. The green substance which started to precipitate at the beginning became yellow-orange under reflux. After 2.5 h of reflux the mixture was allowed to cool and the yellow-orange product filtered off, washed with small portions of hot dry methanol and dried *in vacuo*. Yield *ca.* 65% (Found: C, 37.20; H, 2.45; Cu, 19.65; N, 8.65). Crystals suitable for X-ray analysis were obtained by slow crystallization from water–dioxane (1:5 v/v).

Physical Measurements.—The magnetic susceptibility of a polycrystalline sample of the green isomer of compound **1** was measured by the Faraday method in the temperature range 4.2–290 K using a sensitive RG-HV electrobalance. The field applied was 6.25 kOe. The magnetic susceptibility of a polycrystalline sample of the yellow-orange isomer was measured by the Gouy method in the temperature range 77–290 K using a sensitive RM-2 Cahn electrobalance, at a magnetic field strength of 9.9 kOe. The calibrant employed in both cases was $Hg[Co(SCN)_4]$, the magnetic susceptibility of which was taken[26] as 16.44×10^{-6} cm^3 g^{-1}. All of the measured susceptibilities were corrected for diamagnetism of the constituent atoms calculated by the use of Pascal's constants[27] and found to be -354×10^{-6} cm^3 mol^{-1} for both isomers. The value 60×10^{-6} cm^3 mol^{-1} was used for the temperature-independent paramagnetism of copper(II). The magnetism of the samples was found to be field independent. The exchange parameters were determined by the least-squares procedure and minimization of the function (5) was the criterion used to

$$R = \sum_i \frac{(\chi_i^{\text{exptl}} - \chi_i^{\text{calc}})^2}{(\chi_i^{\text{exptl}})^2} \qquad (5)$$

determine the best fit. The effective magnetic moment was calculated from the equation $\mu_{\text{eff}} = 2.83(\chi_{\text{Cu}}T)^{\frac{1}{2}}$.

The ESR spectra of polycrystalline samples at room temperature and 77 K were recorded on a JEOL-Me X-band spectrometer using a nuclear magnetometer (MJ 110R) and microwave frequency meter (JES-SH-30X) and ESR standards. The spectrum at liquid-helium temperature was measured with a X-band Radiopan SE/X 2543 spectrometer. Solid diphenylpicrylhydrazyl (dpph) was used as the reference and the magnetic field was calibrated with proton and lithium probes.

The IR spectra in the region 400–4000 cm^{-1} were measured in Nujol mulls with a Specord 75 IR spectrophotometer and as KBr pellets with a Perkin-Elmer 180 spectrophotometer. Spectra obtained from the two instruments did not show significant differences. The FIR spectra were measured in Nujol mulls on a Perkin-Elmer 180 spectrophotometer in the range 30–500 cm^{-1}.

The electronic spectra of the solid complexes diluted in Li_2CO_3 were measured in the 200–700 nm region on a Hitachi model 356 spectrophotometer and those of undiluted samples were recorded at 400–2000 nm on a Beckman UV 5240 spectrophotometer. Spectra obtained from the two instruments did not show significant differences.

Crystal and Molecular Structures of $[Cu_2(bipyo)_2Cl_4]$ *Isomers.—Data collection.* Irregularly shaped crystals of average dimension 0.25 mm (0.20 × 0.25 × 0.35 mm for the green isomer of **1**, and 0.25 × 0.20 × 0.30 mm for the yellow-orange isomer) were used for data collection. Preliminary crystallographic data were obtained from oscillation and Weisenberg photographs and were refined by using the positions of 15 reflections centred on a Syntex $P2_1$ instrument. Intensity measurements were carried out on the Syntex $P2_1$ four-circle computer-controlled diffractometer using graphite-monochromated Cu-K_α radiation ($\lambda = 1.541\,78$ Å) and a scintillation counter. 1614 Independent reflections were collected for the green isomer in the range $0 \leqslant 2\theta \leqslant 55°$ and 1366 with $I \geqslant 3\sigma(I)$ were used in the analysis. For the yellow-orange isomer, 1754 independent reflections were collected in the range $0 \leqslant 2\theta \leqslant 55°$ and 1283 with $I \geqslant 3\sigma(I)$ were used in the analysis. The θ–2θ scanning technique with a variable scan speed (4.88–29.3° min^{-1}) was used in both cases. Two check reflections at intervals of 100 were measured and no significant intensity changes were observed. Lorentz and polarization corrections were applied in the usual way. Since the crystals were nearly cylindrical no absorption corrections were made ($\mu = 68.9$ cm^{-1}, $\mu R = 0.9$, where R is the cylinder radius of the crystal).

Crystal data. Green isomer, $C_{20}H_{16}Cl_4Cu_2N_4O_4$, $M = 645.28$, triclinic, space group $P\bar{1}$, $a = 8.664(2)$, $b = 8.732(2)$, $c = 9.099(3)$ Å, $\alpha = 95.62(2)$, $\beta = 107.04(2)$, $\gamma = 114.05(2)°$, $U = 582.1(3)$ Å^3, $D_m = 1.83$ g cm^{-3}, $Z = 1$, $D_c = 1.84$ g cm^{-3}, $F(000) = 322$.

Yellow-orange isomer, monoclinic, space group $P2_1/c$, $a = 7.912(2)$, $b = 9.878(2)$, $c = 15.086(3)$ Å, $\beta = 99.86(2)°$, $U = 1161.6(4)$ Å^3, $D_m = 1.84$ g cm^{-3}, $Z = 2$, $D_c = 1.84$ g cm^{-3}, $F(000) = 644$.

Structure solution and refinement. The structures of both isomers were solved using the heavy-atom method and refined by full-matrix anisotropic least-squares methods for all non-hydrogen atoms (hydrogen atoms were calculated). Calculations were performed with the SHELX 76 program system.[28] The final positional parameters of the non-hydrogen atoms are listed in Table 1. The structure of the green isomer was refined to $R = 0.054$, $R' = 0.064$ $\{w = k[\sigma^2(F_o) + gF_o^2]$, $k = 1.0000$, $g = 0.009\,362\}$ for 154 parameters (data/parameter ratio = 8.87:1). The structure of the yellow-orange isomer was refined to $R = 0.063$, $R' = 0.064$ $\{w = k[\sigma^2(F_o) + gF_o^2]$, $k = 2.8811$, $g = 0.001\,699\}$ for 154 parameters (data/parameter ratio = 8.33:1). Final Fourier difference maps showed peaks with $\Delta\rho_{\text{max/min}} = 0.55/-1.16$ e Å^{-3} for the green isomer and $\Delta\rho_{\text{max/min}} = 1.7$ (*ca.* 1 Å from the Cu atom)/-0.84 e Å^{-3} for the yellow-orange isomer.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

References

1 W. H. Watson, *Inorg. Chem.*, 1969, **8**, 1879 and refs. therein.
2 P. G. Simpson, A. Vinciguerra and J. V. Quagliano, *Inorg. Chem.*, 1963, **2**, 282.
3 A. Vinciguerra, P. G. Simpson, Y. Kakiuti and J. V. Quagliano, *Inorg. Chem.*, 1963, **2**, 286.
4 S. K. Madan and W. E. Bull, *J. Inorg. Nucl. Chem.*, 1964, **26**, 2211.
5 E. J. Halbert, C. M. Harris, E. Sinn and G. J. Sutton, *Aust. J. Chem.*, 1973, **26**, 951.
6 P. Baran, D. Valigura, M. Koman and J. Mroziński, *Proc. 12th Conf. Coord. Chem.*, Bratislava-Smolenice, 1989, p. 437.
7 A. W. Addison, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.
8 J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley and S. Y. Tyree, *J. Am. Chem. Soc.*, 1961, **83**, 3770.
9 W. E. Hatfield and J. C. Morrison, *Inorg. Chem.*, 1966, **5**, 1390.
10 R. Whyman and W. E. Hatfield, *Inorg. Chem.*, 1967, **6**, 1859.
11 R. Whyman, D. B. Copley and W. E. Hatfield, *J. Am. Chem. Soc.*, 1967, **89**, 3135.
12 D. R. Johnson and W. H. Watson, *Inorg. Chem.*, 1971, **10**, 1070.
13 D. R. Johnson and W. H. Watson, *Inorg. Chem.*, 1971, **10**, 1281.
14 J. C. Morrow, *J. Cryst. Mol. Struct.*, 1974, **4**, 243.
15 E. D. Estes and D. J. Hodgson, *Inorg. Chem.*, 1976, **15**, 348.
16 J. A. Paulson, D. A. Krost, G. L. McPherson, R. D. Rogers and J. L. Atwood, *Inorg. Chem.*, 1980, **19**, 2519.
17 M. Gawron, R. C. Palenik and G. J. Palenik, *Acta Crystallogr., Sect. C*, 1988, **44**, 168.

18 R. J. Williams, W. H. Watson and A. C. Larson, *Acta Crystallogr., Sect. B*, 1975, **31**, 2362.

19 R. S. Sager and W. H. Watson, *Inorg. Chem.*, 1968, **7**, 2035.

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

21 B. E. Mayers, L. Bergerand and S. A. Friedberg, *J. Appl. Phys.*, 1969, **40**, 1149.

22 J. S. Smart, *Effective Field Theories of Magnetism*, Saunders, Philadelphia, 1966.

23 B. Bleaney and K. Bowers, *Proc. R. Soc. London, Ser. A*, 1952, **214**, 451.

24 E. J. Halbert, C. M. Harris, E. Sinn and G. J. Sutton, *Aust. J. Chem.*, 1973, **26**, 951.

25 T. P. E. Auf Der Heyde, C. S. Green, D. E. Needham, D. A. Thornton and G. M. Watkins, *J. Mol. Struct.*, 1981, **70**, 121.

26 B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 1958, 4190.

27 E. König, *Magnetic Properties of Coordination and Organometallic Transition Metal Compounds*, Springer, Berlin, 1966.

28 G. M. Sheldrick, SHELX 76 Program for Crystal Structure Determination, University of Cambridge, 1976.

Received 12*th December* 1990; *Paper* 0/05596D