

990. 2,2'-Bipyridylamine Complexes of Copper(II).

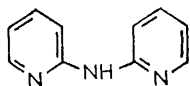
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The behaviour of the copper(II)-2,2'-bipyridylamine (bipyam) system resembles that of the copper(II)-2,2'-bipyridyl system in some respects. The complexes $\text{Cu}(\text{bipyam})_2\text{Cl}_2$, $\text{Cu}(\text{bipyam})_2\text{I}(\text{ClO}_4)$, $\text{Cu}(\text{bipyam})_2(\text{NCS})(\text{ClO}_4)$, $\text{Cu}(\text{bipy})(\text{bipyam})(\text{NO}_3)_2$, and $[\text{Cu}(\text{bipyam})(\text{OH})(\text{ClO}_4)]_2$ have been prepared. The last-mentioned is probably a hydroxo-bridged dimer; the other compounds are believed to contain five-co-ordinate copper; hexa-co-ordination is not entirely eliminated by the spectroscopic data. The solid-state spectra of $\text{Cu}(\text{bipyam})_2(\text{ClO}_4)_2$ and $\text{Cu}(\text{bipyam})_2(\text{NO}_3)_2$ are consistent with a square-planar arrangement of ligands.

Spectra of solutions in water and nitromethane are considered; the behaviour of $\text{Cu}(\text{bipyam})_2(\text{ClO}_4)_2$ in the latter solvent is complex, with at least two non-planar copper(II) species in equilibrium.

Zinc(II) failed to give potentially five-co-ordinate species; preparation of $\text{Zn}(\text{bipyam})_2(\text{ClO}_4)_2$ and $\text{Zn}(\text{bipyam})\text{I}_2$ is recorded.

SOLUTION spectra of some of the complexes¹ of copper(II) chloride with 2,2'-bipyridylamine (I) have been recorded.² Block and his colleagues³ examined various zinc derivatives of the ligand and the ease of removal of the 1-imino-hydrogen atoms from bis-2,2'-bipyridylaminopalladium(II) perchlorate has been demonstrated.⁴ Preparation of potentially five-co-ordinate complexes of copper(II), similar⁵ to $\text{Cu}(\text{bipy})_2\text{I}^+$, with this ligand are described in the present Paper.



EXPERIMENTAL

Perkin-Elmer spectrophotometers models 137 and 237 were used to record infrared spectra for Nujol or hexachlorobutadiene mulls. Diffuse reflectance spectra between 350 and 1000 μ were obtained against a magnesium carbonate blank with a Unicam S.P. 500 spectrophotometer; for solution spectra 1 cm. silica cells and a Unicam S.P. 700 recording spectrophotometer were used. Conductance measurements were made at 25.1° with a Pye Kohlrausch universal bridge (7401), a 1 kc./sec. oscillator, and a cathode ray detector. (The apparatus was rather insensitive to resistances above 8000 ω .)

Light's 2,2'-bipyridylamine was recrystallised from light petroleum ether (b. p. 100—120°) to m. p. 95° (lit.,¹ 95°). All the complexes were dried *in vacuo* over phosphorus pentoxide.

Bis-2,2'-bipyridylaminocopper(II) chloride was prepared as described in ref. 1; it was recrystallised from water (Found: C, 49.7; H, 3.8; Cl, 14.8; Cu, 13.7. Calc. for $\text{C}_{20}\text{H}_{18}\text{Cl}_2\text{CuN}_6$: C, 50.4; H, 3.8; Cl, 14.9; Cu, 13.3%).

Bis-(2,2'-bipyridylamine)copper(II) Perchlorate.—2,2'-Bipyridylamine (0.34 g.) in acetone (5 ml.) was added to copper perchlorate hexahydrate (0.37 g.) in acetone (5 ml.); green crystals of a *diacetate* separated [Found: Cu, 8.7; COMe_2 , 14.3 (by wt. loss). $\text{C}_{20}\text{H}_{18}\text{Cl}_2\text{CuN}_6\text{O}_8 \cdot 2\text{COMe}_2$ requires Cu, 8.8; COMe_2 , 16.1%], $\nu(\text{CO})$ 1695 cm^{-1} . The solvate readily lost acetone on recrystallisation from water or heating to 80°. The resulting *complex* (0.44 g.) formed blue plates (Found: C, 39.7; H, 3.0; N, 12.7; Cu, 10.4. $\text{C}_{20}\text{H}_{18}\text{Cl}_2\text{CuN}_6\text{O}_8$ requires C, 39.8; H, 3.0; N, 13.9; Cu, 10.5%).

Bis-(2,2'-bipyridylamine)copper(II) Nitrate.—2,2'-Bipyridylamine (0.34 g.) in acetone (5 ml.) was mixed with a solution of copper nitrate trihydrate (0.24 g.) in acetone (5 ml.). The bright green solid was recrystallised from water to give olive-green crystals (0.34 g.) of the *complex* (Found: C, 44.7; H, 3.6; N, 20.2; Cu, 11.2. $\text{C}_{20}\text{H}_{18}\text{CuN}_8\text{O}_6$ requires C, 45.3; H, 3.4; N, 21.2; Cu, 11.9%).

¹ Kirschner, *Inorg. Synth.*, 1957, **5**, 14.

² Meibohm, Bellman, and Leth, *Proc. Indiana Acad. Sci.*, 1957, **66**, 95 (*Chem. Abs.*, **52**, 13,721b).

³ Ocone, Soulen, and Block, *J. Inorg. Nuclear Chem.*, 1960, **15**, 71; Block, Roth, and Simkin, *ibid.*, 1960, **16**, 48; Simkin and Block, *ibid.*, 1961, **23**, 253; Block and Simkin, *Inorg. Chem.*, 1963, **2**, 688.

⁴ Geldard and Lions, *J. Amer. Chem. Soc.*, 1962, **84**, 2262.

⁵ Harris, Lockyer, and Waterman, *Nature*, 1961, **192**, 424.

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Iodobis-(2,2'-bipyridylamine)copper(II) Perchlorate.—A solution of 2,2'-bipyridylamine (0.34 g.) and sodium iodide (0.14 g.) in acetone (5 ml.) was added to copper perchlorate hexahydrate (0.37 g.) in acetone (5 ml.); a deep green solid *salt* was slowly deposited, and was recrystallised from water (Found: C, 38.1; H, 2.8; I, 19.4; N, 12.6; Cu, 10.3. $C_{20}H_{18}ClCuIN_6O_4$ requires C, 38.3; H, 2.9; I, 20.0; N, 13.3; Cu, 10.0%).

Thiocyanatobis-(2,2'-bipyridylamine)copper(II) Perchlorate.—Boiling solutions of 2,2'-bipyridylamine (0.34 g.) and ammonium thiocyanate (0.08 g.) in acetone (5 ml.), and of copper perchlorate hexahydrate (0.37 g.) in acetone (5 ml.) were mixed; green crystals of the *perchlorate*, deposited from the solution, were recrystallised from water [Found: C, 45.5; H, 3.3; N, 18.6; Cu, 11.4. $C_{21}H_{18}ClCuN_7O_4S$ requires C, 44.7; H, 3.2; N, 17.4; Cu, 11.1%. Calc. for $(bipyam)_2Cu(NCS)_2$: C, 51.6; H, 3.5; N, 21.9; Cu, 12.4%].

2,2'-Bipyridyl-2,2'-bipyridylaminocopper(II) Nitrate.—An acetone (5 ml.) solution of 2,2'-bipyridyl (0.15 g.) and 2,2'-bipyridylamine (0.17 g.) was added to copper nitrate trihydrate (0.24 g.) in acetone (5 ml.); a pale green solid *complex* was deposited [recrystallisation of this from water caused disproportionation to $Cu(bipyam)_2(NO_3)_2$ and $Cu(bipy)_2(NO_3)_2$] [Found (original product): C, 46.8; H, 3.7; N, 18.3; Cu, 12.3. $C_{20}H_{17}CuN_7O_6$ requires C, 46.6; H, 3.3; N, 19.0; Cu, 12.3%]. Infrared bands characteristic of both ligands were observed. A similar experiment with copper perchlorate gave a mixture on recrystallisation.

Di- μ -hydroxodi-2,2'-bipyridylaminedicopper(II) Perchlorate.—Reaction of 2,2'-bipyridylamine (0.17 g.) and copper perchlorate hexahydrate (0.37 g.) in a boiling aqueous buffer solution (pH 9.27) gave, on cooling, a blue solid *complex* ν 3640 cm^{-1} [Found: C, 35.7; H, 2.9; N, 11.9; Cu, 18.6. $(C_{10}H_{10}ClCuN_3O_3)_2$ requires C, 34.2; H, 2.9; N, 12.0; Cu, 18.1%].

Bis-(2,2'-bipyridylamine)zinc(II) Perchlorate.—2,2'-Bipyridylamine (0.36 g.) and zinc perchlorate hexahydrate (0.36 g.) in acetone (10 ml.) gave a white solid *complex*, which recrystallised from water as bluish-white plates (0.63 g.) (Found: C, 39.2; H, 3.2. $C_{20}H_{18}Cl_2N_6O_8Zn$ requires C, 39.6; H, 3.0%).

2,2'-Bipyridylaminenezinc(II) Iodide.—An attempt to prepare $[Zn(bipyam)_2I]ClO_4$ by reaction of 2,2'-bipyridylamine (0.34 g.), zinc perchlorate hexahydrate (0.36 g.), and sodium iodide (0.15 g.) in acetone (10 ml.) yielded a white solid (0.30 g.) which, after recrystallisation from water, proved to be $Zn(bipyam)_2I_2$ (Found: C, 24.6; H, 1.9; I, 51.6. Calc. for $C_{10}H_9I_2N_6Zn$: C, 24.5; H, 1.9; I, 51.8%). No trisbipyridylaminocopper(II) complex was isolated.

RESULTS AND DISCUSSION

Solution Spectra.—(a) 30,000—8000 cm^{-1} (see Table 1 (a)). The general similarity of the spectra of the green solutions of $Cu(bipyam)_2X_2$ ($X = Cl^-$, NO_3^- , or ClO_4^-) and $Cu(bipyam)_2I(ClO_4)$ implies similar environments for the copper(II) ions in these solutions. Jørgensen⁶ has suggested a non-planar configuration for the bidentate ligands in aqueous ethanolic solutions of bis-2,2'-bipyridylcopper(II) ions; the intensities of the bipyridylaminocopper(II) bands are more compatible with square-planar or tetragonal copper(II), the species *trans*- $Cu(bipyam)_2(H_2O)_2^{2+}$ being most likely.

$Cu(bipyam)_2I(ClO_4)$ absorbs more intensely in nitromethane than in water; $Cu(bipyam)_2(NCS)(ClO_4)$ behaves similarly. Molar conductivities (Λ_M) of 70—80 ohm^{-1} for uni-univalent electrolytes in nitromethane have been suggested,⁷ but more recent literature⁸ suggests a revised range of 50—90 ohm^{-1} . Extrapolation of Λ_M values obtained to infinite dilution for $Cu(bipyam)_2X(ClO_4)$ ($X = I$ or NCS) give Λ_0 values of approximately 66 ohm^{-1} , which certainly indicate 1:1 electrolytes. Measurement of Λ_M at two concentrations is desirable for nitromethane solutions. The spectra are consistent with an absorbing species $Cu(bipyam)_2X^+$ ($X = I$ or NCS), but the co-ordination number of the copper ion may well be six through solvation.

The spectrum of $Cu(bipyam)_2(ClO_4)_2$ in nitromethane is complex. Small amounts of

⁶ Jørgensen, *Acta Chem. Scand.*, 1955, **9**, 1362.

⁷ Harris, Hyholm, and Phillips, *J.*, 1960, 4379.

⁸ Donoghue and Drago, *Inorg. Chem.*, 1963, **2**, 1158; Davison, Edelstein, Holm, and Maki, *ibid.*, p. 1228.

TABLE I.
Solution spectra.
(a) 30,000—8000 cm.⁻¹.

Complex	Concn. (10 ⁻³ M)	Λ_M (25.1°)	Maxima (m μ) with apparent ϵ_M				
<i>In H₂O:</i>							
Cu(bipyam) ₂ Cl ₂	2.47	—	1015(40)	671(46)	602(41)		417(161)
Cu(bipyam) ₂ (NO ₃) ₂	6.58	—	1008(23)	674(40) *	643(41) *	599(40) *	428(155)
Cu(bipyam) ₂ I(ClO ₄)	4.49	—	1042(22)	671(41)		588(41)	420(161)
Cu(bipyam) ₂ (ClO ₄) ₂	3.24	—	1026(22)	692(33) *	668(43) *	599(40) *	428(157)
<i>In MeNO₂:</i>							
Cu(bipyam) ₂ (ClO ₄) ₂	2.73	96	833(71)	645(173)	526(215)	400(351)	381(411)
(Sat ^d . w. NaClO ₄)	2.73	—	971(57)	625(180)	544(227)	400(300)	380(373)
Cu (bipyam) ₂ (ClO ₄) ₂ ...	1.43	99	833(73)	637(128)	507(331)	395(453)	384(498)
" ..	0.63	112	840(181)	—	498(875)	397(918)	384(1000)
Cu(bipyam) ₂ (NCS)ClO ₄	3.90	45	957(44)	685(149)			
" ..	0.78	55					407(1064)
Cu(bipyam) ₂ IClO ₄	7.50	46	1013(44)	658(97)			
" ..	1.50	58					389(971) *

(b) Ultraviolet spectra.

Complex	Concn. (10 ⁻⁵ M)	$\lambda(\epsilon_1)$	$\lambda(\epsilon_2)$
<i>In EtOH:</i>			
2,2'-Bipyridylamine	3.55	314.5(1.6 × 10 ⁴)	265.6(2.5 × 10 ⁴)
<i>In H₂O:</i>			
Cu(ClO ₄) ₂ (2-bipyam)	1.10 †	318.4(2.5 × 10 ⁴) 297.6(1.9 × 10 ⁴)sh	249.7(2.6 × 10 ⁴)
Cu(bipyam) ₂ (ClO ₄) ₂	—	318 296sh	248
Cu(bipyam) ₂ (NO ₃) ₂	3.3	316(2.6 × 10 ⁴) 297(2.1 × 10 ⁴)sh	250(2.8 × 10 ⁴)
	1.2	317(2.6 × 10 ⁴) 297(2.0 × 10 ⁴)sh	248(2.8 × 10 ⁴)

* Very broad. † Concn. of copper(II) perchlorate.

Cu(bipyam)₂(NCS)ClO₄ was insufficiently soluble in water, and Cu(bipyam)₂(NO₃)₂ and Cu(bipyam)₂Cl₂ in nitromethane, at room temperature for spectra to be obtained.

the solid may be recrystallised from the solvent with no change in the infrared spectrum; the boiling concentrated solutions are blue-black, but dilution changes the colour through purple-red to almost pure red (0.6 × 10⁻³M). Conductance measurements and the behaviour in the presence of an excess of sodium perchlorate [Table 1(a)] suggest that the following equilibrium could be important:



The precise nature of the perchlorate association is difficult to estimate, but the intensity of the spectra implies the absence of square-planar or tetragonal species, in fact a tetrahedral complex ion may exist in the more dilute solutions. The maxima between 500 and 380 m μ are sufficiently intense to be "redox" bands, but the 840 m μ maximum (0.6 × 10⁻³) is assigned as a *d-d* band, and a tetrahedral species would be expected to give a more intense band at longer wavelength than a corresponding planar species [cf. Cu(bipyam)₂(ClO₄)₂ in water].

(b) *Ultraviolet spectra* (see Table 1(b)). Splitting of the 314.5 m μ maximum of 2,2'-bipyridylamine occurs in the presence of copper(II) ions, but there is no marked bathochromic shift of these maxima as in the bipyridyl case.⁹ The shorter-wavelength maximum (265.6 m μ) undergoes a hypsochromic shift; these results are consistent with co-ordination to the heterocyclic nitrogen atoms.

⁹ Martin, McWhinnie, and Waind, *J. Inorg. Nuclear Chem.*, 1961, **23**, 207.

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Solid-state Spectra (see Tables 2 and 3).—The N-H stretching mode for the 2,2'-bipyridylamine complexes is observed between 3300 and 3320 cm^{-1} with no increase in intensity; only in the case of $\text{Cu}(\text{bipyam})_2(\text{NO}_3)_2$ are the relative intensities between 3000

TABLE 2.
Diffuse reflectance spectra.

	(Reflectance minima— $\text{m}\mu$.)			
$\text{Cu}(\text{bipyam})_2\text{Cl}_2$ (greenish-brown)	360s	445m-s	725m-s	985m
$\text{Cu}(\text{bipyam})_2(\text{ClO}_4)_2$ (deep blue)	375m, infl		555s	935w
$\text{Cu}(\text{bipyam})_2(\text{NO}_3)_2$ (olive-green)	350s	425s	565m	
$\text{Cu}(\text{bipyam})_2\text{I}(\text{ClO}_4)$ (deep green)		420s	710s	960m
$\text{Cu}(\text{bipyam})(\text{NCS})\text{ClO}_4$ (deep green)	365s	425s, infl	625s	925m
$\text{Cu}(\text{bipy})(\text{bipyam})(\text{NO}_3)_2$ (pale green)		445m-s	695s	990s

TABLE 3.
Infrared spectra—anionic species

	$\text{CuL}_2(\text{ClO}_4)_2$	$\text{CuL}_2(\text{NO}_3)_2$	$\text{CuL}_2\text{I}\cdot\text{ClO}_4$	$\text{CuL}_2\text{NCS}\cdot\text{ClO}_4$	$\text{CuL}(\text{bipy})(\text{NO}_3)_2$	$\text{Cu}(\text{py})_2(\text{NCS})_2$
ClO_4^-	1120s 1095s 1077s 934w	—	1112s 1096s 1077s 935w	1110s 1096s 1080s, sh 935w	—	—
NO_3^-	—	1395s 1380s 1365s, sh 825m 715m	—	—	1380s, b 810w	—
$-\text{O}-\text{NO}_2\cdots$	—	—	—	—	1465s 1280s 1015s 832m	—
NCS	—	—	—	2096s 2075s 810w	—	2109m 2100s 2050m

s = Strong; m = medium; w = weak; b = broad.

and 3500 cm^{-1} altered from those of the free base. The slight shift of some bipyridylamine bands in the complexes are characteristic of co-ordination through the pyridyl-nitrogen atoms. There was no obvious correlation between the C-H out-of-plane deformation mode and stereochemistry.

The reflectance spectra (see Figure) of $\text{Cu}(\text{bipyam})_2(\text{ClO}_4)_2$ and $\text{Cu}(\text{bipyam})_2(\text{NO}_3)_2$ are those expected for square-planar or tetragonal copper(II). The nitrate and the perchlorate group are ionic, as shown by the infrared spectra (some splitting of the broad perchlorate band at 1100 cm^{-1} cannot indicate co-ordination in the absence of intensity for ν_1 at 934 cm^{-1}).

The reflectance spectra of $\text{Cu}(\text{bipyam})_2\text{Cl}_2$, $\text{Cu}(\text{bipyam})_2\text{I}\cdot\text{ClO}_4$, and $\text{Cu}(\text{bipyam})_2(\text{NCS})\text{ClO}_4$ are all rather similar and resemble that of $\text{Cu}(\text{bipy})(\text{bipyam})(\text{NO}_3)_2$. The perchlorate groups are ionic, the thiocyanato-group is co-ordinated,¹⁰ possibly to nitrogen,¹¹ and the mixed ligand complex has one co-ordinated¹² and one ionic nitrate group.

General Discussion.—The blue product of reaction between copper perchlorate and 2,2'-bipyridylamine at pH 9.2 is formulated as the hydroxo-bridged dimer $[\text{Cu}(\text{bipyam})(\text{OH})\text{ClO}_4]_2$, after the 2,2'-bipyridyl analogue¹³ (OH, 3640; ClO_4^- , 1116, 1095, 1076s, b, 932 cm^{-1} w—m).

¹⁰ Chatt and Duncanson, *Nature*, 1956, **178**, 997.

¹¹ Lewis, Nyholm, and Smith, *J.*, 1961, 4590.

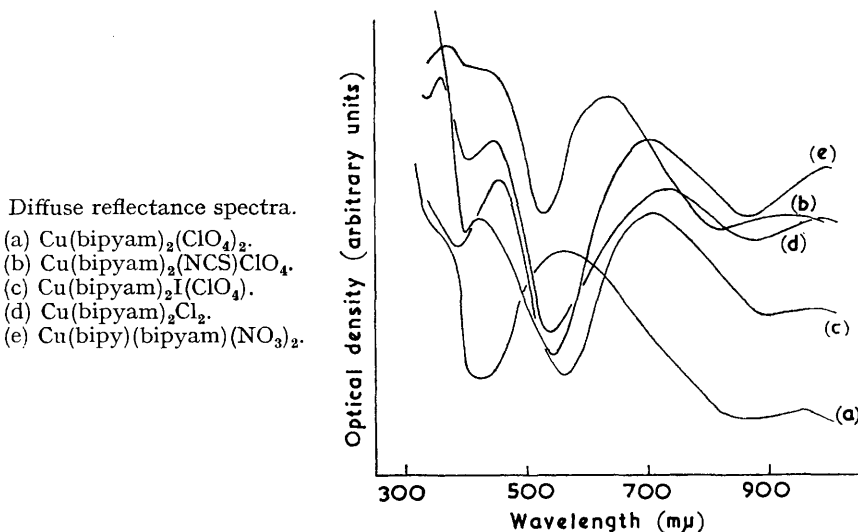
¹² (a) Gatehouse, Livingstone, and Nyholm, *J.*, 1957, 4222; (b) Bannister and Cotton, *J.*, 1960, 2276.

¹³ McWhinnie, *J.*, 1964, 2959.

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The iodo- and thiocyanato-groups of $\text{Cu}(\text{bipyam})_2\text{I}\cdot\text{ClO}_4$ and $\text{Cu}(\text{bipyam})_2(\text{NCS})(\text{ClO}_4)$ are co-ordinated in nitromethane solution and, certainly in the latter case, in the solid state. The distinction made between bridging and unidentate thiocyanato-groups by Chatt and Duncanson¹⁰ appears to be of general application, in which case the thiocyanate group would be unidentate in $\text{Cu}(\text{bipyam})_2(\text{NCS})(\text{ClO}_4)$, giving the cupric ion a co-ordination number five; the issue is made less certain by the observation of NCS^- bands around 2100 cm^{-1} (Table 3) for $\text{Cu}(\text{py})_2(\text{NCS})_2$, which has been shown¹⁴ to contain bridging thiocyanate groups.

Both uni- and bi-dentate nitrate belong to point group C_{2v} , consequently observation of one co-ordinated nitrate group in $\text{Cu}(\text{bipy})(\text{bipyam})(\text{NO}_3)_2$ does not necessarily imply a co-ordination number five, especially as bidentate nitrate is not unknown,¹⁵ because



infrared results are unable to differentiate between the two possibilities. The general similarities of the solid-state spectra of $\text{Cu}(\text{bipyam})_2\text{X}(\text{ClO}_4)$ ($\text{X} = \text{I}^-$ or NCS^-), $\text{Cu}(\text{bipyam})_2\text{Cl}_2$, and $\text{Cu}(\text{bipy})(\text{bipyam})(\text{NO}_3)_2$ imply similar solid-state structures.

Four solid-state structures must be considered: (a) dimers of the type $(\text{bipyam})_2\text{CuX}_2\text{Cu}(\text{bipyam})_2^{2+}$; (b) trigonal bipyramidal as for $\text{Cu}(\text{bipy})_2\text{I}^+$; ¹⁶ (c) square-pyramidal; and (d) a polymeric structure based on (c). Neither (a) nor (d) persists in nitromethane solutions of $\text{Cu}(\text{bipyam})_2\text{X}(\text{ClO}_4)$ ($\text{X} = \text{I}^-$ or NCS^-). In structures (b) and (c) the copper(II) ions have ligand fields of idealised symmetry C_{2v} and C_{4v} , respectively, and more intensity would be expected in the spectra than for copper(II) in D_{4h} symmetry, *e.g.*, (d). In fact, the longer-wavelength bands for the four complexes $\text{Cu}(\text{bipyam})_2\text{X}(\text{ClO}_4)$ ($\text{X} = \text{I}$ or NCS), $\text{Cu}(\text{bipyam})_2\text{Cl}_2$, and $\text{Cu}(\text{bipy})(\text{bipyam})(\text{NO}_3)_2$ all show more intensity, relatively, than the corresponding band of $\text{Cu}(\text{bipyam})_2(\text{ClO}_4)_2$ (Figure), which would favour (b) and (c); but greater intensity than observed would make these arguments more compelling. With the spectroscopic data available, it does not appear possible to differentiate between (b) and (c), or to eliminate entirely structures containing hexaco-ordinate copper.

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¹⁴ Porai-Koshits and Tishchenko, *Krystallografiya*, 1959, **4**, 239.

¹⁵ Cotton and Soderberg, *J. Amer. Chem. Soc.*, 1963, **85**, 2402.

¹⁶ Barclay, Hoskins, and Kennard, *J.*, 1963, 5691.