1086. *The Crystal Structure of Iodobis-(2,2′-bipyridyl)copper*(II) *Iodide.*

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Iodobis-(2,2′-bipyridyl)copper(II) iodide, $Cu(C_{10}H_8N_2)_2I_2$, crystallises in the triclinic system with two molecules in the unit cell of dimensions a = 10·66 ± 0·05, b = 14·37 ± 0·05, c = 7·44 ± 0·05 Å, α = 93·3 ± 0·5°, β = 101·1 ± 0·5°, γ = 107·6 ± 0·5°. The atoms were located from three-dimensional Patterson and Fourier syntheses; refinement was by the method of least squares. The crystal is built of positively charged iodobis-(2,2′-bipyridyl)copper(II) ions and negatively charged iodide ions. The copper atom is surrounded by four nitrogen atoms and an iodine atom at the corners of a slightly distorted trigonal bipyramid. The iodine atom and two nitrogen atoms (from two different bipyridyl molecules) are in a plane containing the copper atom. The other two nitrogen atoms lie on a line (passing through the copper atom) which makes an angle of 9° with the normal to this plane. All five atoms are at normal covalent distances from the copper atom.

The compounds $Cu(bipy)_2(ClO_4)_2$ and $Cu(phen)_2(ClO_4)_2$, which are formed between 2,2′-bipyridyl and 1,10-phenanthroline, respectively, and copper(II) perchlorate, react with halide ions in nitrobenzene or nitromethane solutions to form monohalogenobis(chelate)-copper(II) ions. Crystalline compounds of the types $[Cu(phen)_2X]ClO_4$ (X = Cl, Br, I, SCN, NO_2, $H{\cdot}CO_2$, OAc, and OBz) and $[Cu(bipy)_2X]ClO_4$ (X = Cl, Br, I, and SCN^-) have been isolated from aqueous-acetone solutions. These compounds behave as uni-univalent electrolytes in nitrobenzene and nitromethane solutions. The complexes $Cu(phen)_2X_2,nH_2O$ (X = Cl, n = 3·5; X = Br and I, n = 1; X = SCN, n = 0; X = $H{\cdot}CO_2$ and OAc, n = 6) and $Cu(bipy)_2X_2,nH_2O$ (X = Cl, n = 6; X = Br, n = 2; X = I and SCN, n = 0) are also uni-univalent electrolytes in nitromethane solution.[1] In the complex ions $[Cu(phen)_2X]^+$ and $[Cu(bipy)_2X]^+$, the copper atom appears to have a co-ordination number of five in non-aqueous solvents unless a solvent molecule occupies the sixth position in an octahedral structure. In the solid state these ions could be octahedral by polymerisation. Nyholm[2] suggested that these ions have a trigonal bipyramidal stereochemistry because of a supposed large orbital contribution to their magnetic moments. Although this structure is correct, it was based on erroneous magnetic-susceptibility measurements; it has since been shown that their moments are normal for copper(II) compounds (1·8—2·0 B.M.).[1]

The crystal-structure determination of iodobis-(2,2′-bipyridyl)copper(II) iodide was

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[1] Harris, Lockyer, and Waterman, *Nature*, 1961, **192**, 424.

[2] Nyholm, 10th Solvay Council, Brussels, 1956, p. 355; Gillespie and Nyholm, *Quart. Rev.*, **1957**, **11**, 376.

undertaken to establish the stereochemical arrangement about the copper atom in the solid state. The iodide was chosen because it was the only simple halogen derivative which could be prepared in an anhydrous form.

STRUCTURE DETERMINATION

Brown crystals of iodobis-(2,2′-bipyridyl)copper(II) iodide were grown at 0° from the solution formed by mixing aqueous-alcoholic solutions of bis-(2,2′-bipyridyl)copper(II) perchlorate and sodium iodide (Found: C, 37·9; H, 2·4; Cu, 9·9; N, 8·8. Calc. for $C_{20}H_{16}CuI_2N_4$: C, 38·1; H, 2·6; Cu, 10·1; N, 8·9%).

Crystal Data.—$C_{20}H_{16}CuI_2N_4$; *M*, 629·7; triclinic; $a = 10{\cdot}66 \pm 0{\cdot}05$, $b = 14{\cdot}37 \pm 0{\cdot}05$, $c = 7{\cdot}44 \pm 0{\cdot}05$ Å, $\alpha = 93{\cdot}3 \pm 0{\cdot}5°$, $\beta = 101{\cdot}1 \pm 0{\cdot}5°$, $\gamma = 107{\cdot}6 \pm 0{\cdot}5°$; $U = 1058$ Å^3; $D_m = 1{\cdot}99$ g. cm.$^{-3}$ (by flotation); $Z = 2$; $D_c = 1{\cdot}98$ g. cm.$^{-3}$; $F(000) = 598$. Space group; $P\bar{1}(C_i^1$ — No. 2), $\mu = 269$ cm.$^{-1}$. Radiation, copper, unfiltered; single-crystal oscillation and Weissenberg photographs.

TABLE 1.

Final atomic co-ordinates.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	r.m.s. e.s.d. (Å)	Atom	*x*/*a*	*y*/*b*	*z*/*c*	r.m.s. e.s.d. (Å)
I(1)	0·3724	0·2800	0·1207	0·004	C(8)	−0·0339	−0·0224	0·7061	0·054
I(2)	−0·1284	0·2334	0·0826	0·003	C(9)	0·0588	0·0644	0·7985	0·058
Cu	−0·1408	0·2280	0·4407	0·006	C(10)	0·0369	0·1481	0·6986	0·041
N(1)	−0·3100	0·1146	0·3652	0·038	C(11)	0·1505	0·3392	0·4790	0·045
N(2)	−0·0844	0·1321	0·5857	0·037	C(12)	0·2687	0·4134	0·5619	0·048
N(3)	0·0383	0·3363	0·5219	0·033	C(13)	0·2591	0·4980	0·6796	0·051
N(4)	−0·2087	0·3243	0·5913	0·035	C(14)	0·1500	0·4920	0·7203	0·047
C(1)	−0·4302	0·1107	0·2665	0·046	C(15)	0·0348	0·4154	0·6400	0·039
C(2)	−0·5358	0·0282	0·2021	0·052	C(16)	−0·1066	0·4091	0·6729	0·048
C(3)	−0·5211	−0·0680	0·2406	0·055	C(17)	−0·1336	0·4851	0·7914	0·052
C(4)	−0·4113	−0·0666	0·3507	0·048	C(18)	−0·2677	0·4652	0·8163	0·051
C(5)	−0·3049	0·0248	0·4226	0·043	C(19)	−0·3641	0·3804	0·7261	0·053
C(6)	−0·1769	0·0376	0·5568	0·049	C(20)	−0·3364	0·3106	0·6116	0·047
C(7)	−0·1580	−0·0425	0·6457	0·047					

TABLE 2.

Final thermal parameters.

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{31}	b_{12}
I(1)	0·0190	0·0094	0·0637	−0·0001	0·0064	0·0084
I(2)	0·0138	0·0049	0·0122	0·0000	0·0030	0·0059
Cu	0·0127	0·0048	0·0185	0·0040	0·0095	0·0043
N(1)	0·0098	0·0075	0·0403	0·0040	−0·0050	0·0027
N(2)	0·0230	0·0075	0·0098	0·0107	−0·0096	0·0076
N(3)	0·0168	0·0055	0·0084	0·0005	0·0040	0·0052
N(4)	0·0166	0·0049	0·0184	0·0006	−0·0034	0·0020
C(1)	0·0087	0·0080	0·0322	0·0124	−0·0135	−0·0036
C(2)	0·0071	0·0238	0·0193	0·0221	0·0281	0·0150
C(3)	0·0414	0·0059	0·0190	0·0039	0·0015	0·0087
C(4)	0·0249	0·0077	0·0157	−0·0115	−0·0324	0·0099
C(5)	0·0245	0·0031	0·0086	−0·0131	−0·0119	0·0010
C(6)	0·0212	0·0082	0·0270	0·0201	0·0132	0·0070
C(7)	0·0263	0·0045	0·0276	0·0110	0·0299	0·0083
C(8)	0·0276	0·0093	0·0424	0·0329	0·0273	0·0148
C(9)	0·0292	0·0091	0·0479	−0·0036	0·0180	0·0213
C(10)	0·0095	0·0080	0·0132	0·0031	−0·0127	0·0088
C(11)	0·0063	0·0116	0·0210	0·0034	−0·0024	−0·0034
C(12)	0·0105	0·0155	0·0202	0·0257	−0·0060	0·0176
C(13)	0·0276	0·0102	0·0289	0·0392	0·0188	0·0177
C(14)	0·0063	0·0094	0·0316	0·0416	−0·0050	0·0079
C(15)	0·0153	0·0022	0·0163	−0·0058	−0·0049	0·0025
C(16)	0·0373	0·0045	0·0124	0·0109	0·0030	0·0119
C(17)	0·0279	0·0107	0·0286	0·0196	0·0288	0·0171
C(18)	0·0320	0·0064	0·0115	0·0017	0·0169	0·0090
C(19)	0·0246	0·0130	0·0217	0·0131	−0·0149	0·0193
C(20)	0·0156	0·0111	0·0264	0·0180	0·0124	0·0188

TABLE 3.

Calculated structure factors and observed structure amplitudes. (Scale: ½ absolute).

l	*F*c	|*F*o|
	0,0,*l*	
1	−4	5
2	18	20
3	−20	24
4	−31	33
5	−23	22
6	−29	33
	0,1,*l*	
−8	−15	12
−7	−9	12
−6	−20	24
−5	23	29
−4	18	23
−3	70	69
−2	75	70
−1	35	35
1	−44	49
2	−75	71
3	−63	65
4	−18	23
5	−12	13
	0,2,*l*	
−6	30	35
−5	38	41
−4	34	39
−3	33	33
−2	−84	84
−1	−35	41
0	−65	66
1	−60	61
2	−41	37
3	15	18
4	29	32
5	24	27
6	25	27
	0,3,*l*	
−8	21	17
−6	19	18
−5	−15	16
−4	−15	18
−3	−76	70
−2	−44	36
−1	−76	79
0	16	16
1	67	53
2	45	45
3	49	48
4	10	9
5	19	19
	0,4,*l*	
−6	−24	25
−5	−36	37
−4	−21	22
−3	−42	42
−2	43	38
−1	64	63
0	79	72
1	37	37
2	8	14
3	−9	13
4	−23	21
6	−22	21
8	−16	14
	0,5,*l*	
−8	−17	15
−7	−12	12
−6	−21	21
−5	11	14
−4	20	20
−3	62	59
−2	42	46
−1	22	31
0	−11	12
1	−44	45
2	−11	12
3	−40	44
5	−20	18
	0,6,*l*	
−6	22	20
−5	35	32
−4	15	18
−3	18	23
−2	−32	35
−1	−29	31
0	−45	47
1	−28	30
3	−13	17
4	18	18
6	14	12
	0,7,*l*	
−8	13	12
−7	13	12
−6	16	14
−4	−15	17
−3	−32	36
−2	−32	35
−1	−12	14
0	−11	14
1	31	30
3	28	27
5	16	15
6	9	9
	0,8,*l*	
−6	−9	10
−5	−30	29
−4	−13	13
−3	−23	22
−2	24	28
−1	15	18
0	27	30
1	12	11
2	−3	8
3	15	16
6	−14	15
	0,9,*l*	
−8	−15	11
−6	−14	12
−3	16	20
−2	28	31
0	12	16
1	−22	22
2	22	24
3	−15	17
6	−16	13
	0,10,*l*	
−6	8	10
−5	23	20
−3	13	14
−2	−11	14
0	−8	10
1	−12	11
	0,11,*l*	
−6	14	12
−3	−12	12
−2	−19	20
−1	16	19
0	−27	27
	0,12,*l*	
−5	−16	14
−3	−15	15
3	18	22
	0,14,*l*	
−1	12	15
	1,−15,*l*	
1	−15	14
	1,−14,*l*	
−1	−20	18
0	−22	20
2	−12	16
3	15	15
	1,−13,*l*	
−3	−21	19
1	15	15
2	28	28
3	19	19
	1,−12,*l*	
−1	21	21
0	38	38
1	13	14
3	−22	25
5	−18	18
	1,−11,*l*	
−3	29	28
−2	19	17
−1	25	26
0	−31	30
1	−18	21
2	−32	33
3	−26	26
	1,−10,*l*	
−6	20	19
−4	16	14
−2	−33	33
−1	−22	21
0	−56	56
2	−15	17
3	19	23
4	15	18
5	19	19
6	17	17
	1,−9,*l*	
−4	−19	15
−3	−42	36
−2	−20	19
−1	−22	23
0	18	18
1	33	37
2	37	40
3	31	37
	1,−8,*l*	
−6	−24	20
−4	−18	16
−2	33	33
−1	38	35
0	64	66
1	17	17
3	−21	25
4	−20	24
6	−18	20
	1,−7,*l*	
−5	16	13
−4	17	17
−3	66	60
−2	22	18
−1	15	17
0	−20	21
1	−44	48
2	44	45
3	−23	23
5	−21	22
	1,−6,*l*	
−6	31	25
−5	25	20
−2	−47	43
−1	−50	52
0	−45	50
1	−4	10
2	−16	22
4	27	35
5	14	14
	1,−5,*l*	
−5	−24	23
−4	−23	19
−3	−51	47
−2	−31	28
−1	16	20
0	29	27
1	43	47
3	63	69
4	−15	20
5	25	23
	1,−4,*l*	
−6	−22	19
−5	−32	26
−4	−19	17
−2	52	49
−1	39	40
0	55	57
1	24	35
2	−23	33
3	−7	16
4	11	12
6	−19	20
	1,−3,*l*	
−5	16	17
−4	26	24
−3	54	53
−2	20	22
−1	16	20
0	−19	20
1	−64	78
2	36	46
3	−41	42
5	−25	25
	1,−2,*l*	
−6	25	27
−5	36	38
−3	11	17
−2	−55	48
0	−40	38
1	13	19
2	−40	40
5	−9	10
6	21	22
	1,−1,*l*	
−8	17	15
−7	14	15
−6	15	16
−5	−19	21
−4	−9	11
−3	−42	43
−2	−23	22
−1	22	21
0	−37	31
1	41	35
2	−6	10
3	9	15
4	6	11
5	20	21
6	20	22
	1,0,*l*	
−9	10	10
−6	−11	15
−5	−34	34
−4	−11	14
−3	−18	24
−2	47	44
−1	21	22
0	39	28
1	−29	27
2	16	20
3	28	30
4	17	19
5	11	17
6	−17	17
7	−10	10
8	−19	16
9	−7	4
	1,1,*l*	
−8	−21	14
−6	−28	28
−5	17	21
−3	23	26
−2	17	18
−1	−30	29
0	29	27
1	18	20
2	39	39
3	−5	12
4	−17	21
5	−25	24
6	−26	24
	1,2,*l*	
−6	11	12
−5	23	24
−3	20	22
−2	7	11
−1	14	17
0	12	10
1	3	7
2	−20	29
3	−44	45
4	−17	19
5	−14	21
	1,3,*l*	
−4	16	18
−2	−17	19
−1	9	9
0	−47	50
1	−28	35
2	−33	31
	1,4,*l*	
−5	−25	23
−3	−33	30
−2	−14	17
−1	−34	33
0	−21	20
2	26	26
3	56	57
	1,5,*l*	
−6	−21	20
−3	−23	25
−1	10	14
0	60	62
1	24	25
2	52	50
	1,6,*l*	
−3	30	34
−2	19	22
−1	49	48
0	26	25
1	−28	33
2	−12	13
3	−58	56
	1,7,*l*	
−4	15	17
−3	24	24
−2	−16	18
0	−52	57
1	−42	47
2	−33	34
	1,8,*l*	
−3	−38	35
−2	−19	22
−1	−43	43
0	−24	25
1	21	23
2	16	19
3	46	47
	1,9,*l*	
−5	−19	16
−3	−34	33
−2	17	20
−1	6	5
0	50	53
1	29	30
2	30	35
	1,10,*l*	
−3	27	29
−2	38	37
−1	17	19
0	20	22
1	−13	16
2	−20	26
3	−26	27
	1,11,*l*	
−5	20	15
−3	13	15
0	−35	35
1	−24	26
2	−18	22
	1,12,*l*	
−3	−18	18
−2	−25	24
−1	−20	20
0	−11	13
1	11	16
3	22	27
	1,13,*l*	
−3	−17	15
1	19	21
	1,14,*l*	
−2	19	18
1	−9	12
3	−13	16
	2,−15,*l*	
1	−13	12
	2,−14,*l*	
−2	−13	14
−1	−14	14
	2,−13,*l*	
−3	−17	18
−1	−12	13
1	13	15
3	16	16
	2,−12,*l*	
−2	17	18
0	23	22
2	12	15
	2,−11,*l*	
−3	25	23
3	−14	14
5	−15	18
	2,−10,*l*	
−6	14	11
−2	−11	13
−1	8	12
0	−17	19
2	−19	21
3	−12	18
4	−10	11
6	18	17
	2,−9,*l*	
−1	9	12
0	19	22
2	−16	19
3	14	19
4	13	16
5	14	13
6	17	18
	2,−8,*l*	
−3	−14	13
−1	−17	17
2	31	34
3	32	34
4	8	10
5	15	20
6	−25	25
	2,−7,*l*	
−6	−18	15
0	48	50
1	17	21
2	31	33
3	−14	12
4	−20	22
5	−36	44
	2,−6,*l*	
−5	17	16
−3	27	23
−2	20	17
−1	44	35
0	−7	12
1	−12	19
2	−43	43
3	−53	58
5	−14	16
6	12	12
	2,−5,*l*	
−8	14	12
−6	21	18
−4	9	11
−3	14	20

TABLE 3. (*Continued.*)

l	F_c	$\lvert F_o \rvert$
−2	−23	23
−1	−20	19
0	−71	69
1	−22	25
2	−46	52
3	22	33
4	9	10
5	42	39
6	22	24
	$2,-4,l$	
−3	−58	65
−2	−19	17
−1	−55	54
0	−7	7
1	29	37
2	42	38
3	67	62
4	22	24
5	16	20
6	−17	16
7	−15	15
	$2,-3,l$	
−6	−20	20
−5	−20	19
−4	−10	10
−3	−19	23
−2	−10	12
−1	50	60
0	110	100
1	58	50
2	45	38
3	−36	29
4	−25	24
5	−31	28
6	−22	22
7	−12	10
	$2,-2,l$	
−5	20	24
−4	6	13
−3	79	77
−2	11	14
−1	101	93
0	4	7
1	−56	52
2	−55	52
3	−77	72
4	−14	17
5	−13	17
6	11	14
	$2,-1,l$	
−8	11	13
−6	25	26
−5	26	30
−4	44	48
−3	28	27
−2	−81	90
−1	−26	27
0	−75	54
1	−63	55
2	−43	47
3	11	10
4	36	39
5	25	26
6	28	28
	$2,0,l$	
−9	11	10
−8	16	14
−6	17	20
−5	−22	24
−4	−7	10
−3	−61	58
−2	−90	100
−1	−38	35
0	−7	7
1	61	61
2	52	54
3	55	57
4	26	32
5	14	18
6	−8	12
7	−12	11
	$2,1,l$	
−7	−11	13
−6	−29	30
−5	−26	30
−4	−28	30
−3	−28	28
−2	9	10
−1	64	64
0	120	105
1	48	48
2	27	29
3	−22	28
4	−26	25
5	−16	17
6	−28	30
	$2,2,l$	
−8	−18	16
−7	−9	10
−6	−23	22
−5	19	18
−4	21	22
−3	62	73
−2	64	71
−1	37	37
0	7	7
1	−55	57
2	−34	34
3	−60	58
4	−13	17
	$2,3,l$	
−6	23	25
−5	42	41
−4	27	25
−3	23	22
−2	−42	40
−1	−41	39
0	−87	90
1	−23	28
2	−22	20
	$2,4,l$	
−8	18	15
−6	19	18
−5	−10	11
−4	−16	16
−3	−59	57
−2	−52	50
−1	−17	18
0	−25	34
1	59	60
2	22	22
3	41	39
	$2,5,l$	
−6	−17	19
−5	−36	33
−4	−20	20
−3	−23	21
−2	33	32
−1	25	24
0	65	69
1	23	26
	$2,6,l$	
−8	−19	13
−6	−17	16
−4	12	13
−3	36	31
−2	48	41
−1	7	10
1	−27	32
3	−27	32
	$2,7,l$	
−6	13	12
−5	30	26
−4	9	9
−3	25	24
−2	−33	33
0	−31	32
1	−18	21
	$2,8,l$	
−6	16	15
−4	−15	14
−3	−24	23
−2	−21	22
−1	−6	11
0	−11	12
1	17	19
	$2,9,l$	
−5	−22	18
−3	−27	25
−2	18	18
−1	11	13
0	8	12
	$2,10,l$	
−6	−14	11
−2	23	24
	$2,12,l$	
0	−13	14
	$3,-15,l$	
0	19	18
	$3,-14,l$	
−1	11	14
1	−16	14
2	−21	21
	$3,-13,l$	
−1	−25	23
0	−28	25
3	15	16
	$3,-12,l$	
−3	−32	32
−1	−21	26
0	13	15
1	20	24
2	27	27
3	29	26
	$3,-11,l$	
−2	24	28
−1	25	25
0	43	42
1	19	21
3	−19	20
	$3,-10,l$	
−3	39	41
−2	25	27
−1	19	22
0	−12	14
1	−40	44
2	−25	29
3	−30	32
	$3,-9,l$	
−2	−31	38
−1	−37	41
0	−50	51
1	−11	16
2	16	20
3	21	25
	$3,-8,l$	
−3	−45	52
−2	−38	42
0	17	21
1	32	35
2	28	34
3	37	40
	$3,-7,l$	
−2	36	39
−1	28	30
0	89	88
1	−2	10
3	−24	25
	$3,-6,l$	
−3	52	57
−2	34	43
−1	16	22
0	−14	15
1	−54	53
2	−23	25
3	−29	32
	$3,-5,l$	
−2	−60	63
−1	−25	28
0	−48	49
1	−5	12
2	−17	22
	$3,-4,l$	
−3	−63	69
−2	−18	24
−1	−7	13
0	13	12
1	32	35
2	9	14
3	31	33
	$3,-3,l$	
−3	−24	32
−2	52	44
−1	31	34
0	46	44
1	4	7
3	14	16
	$3,-2,l$	
−8	−20	21
−6	−17	20
−5	16	21
−4	18	22
−3	41	39
−2	26	26
0	−4	7
1	−28	28
2	5	14
3	−12	17
4	−10	16
5	−21	27
	$3,-1,l$	
−6	21	22
−5	33	36
−3	19	25
−2	−42	33
0	−18	19
2	−7	13
3	−24	24
5	−14	17
6	17	19
	$3,0,l$	
−8	20	19
−7	10	10
−6	20	21
−5	−10	12
−4	−17	20
−3	−16	16
−2	−27	24
−1	9	11
0	−18	18
1	4	11
2	−24	27
3	13	21
5	18	20
6	19	18
	$3,1,l$	
−6	−9	11
−5	−30	30
−4	−6	10
−3	−15	16
−2	16	20
−1	−19	17
1	11	15
3	32	27
	$3,2,l$	
−2	15	15
0	29	27
2	54	47
3	−13	14
5	−22	24
6	−23	21
	$3,3,l$	
−3	19	15
−1	30	28
0	14	14
1	−6	12
2	−18	22
3	−39	36
	$3,4,l$	
−2	−11	12
−1	22	22
0	−63	57
1	−18	17
2	−34	32
	$3,5,l$	
−3	−32	28
−2	−17	16
−1	−26	26
0	−22	24
2	18	22
3	44	42
	$3,6,l$	
−3	−21	20
−2	12	13
0	40	39
1	32	31
2	29	31
	$3,7,l$	
−3	32	32
−2	22	21
−1	31	34
0	20	21
1	−15	17
2	−14	20
3	−37	34
	$3,8,l$	
−3	26	26
0	−37	36
1	−32	32
2	−19	21
	$3,9,l$	
−3	−17	16
−2	−28	27
−1	−25	26
0	−18	20
1	13	16
2	15	16
3	27	27
	$3,10,l$	
−3	−17	15
0	31	32
1	22	22
2	16	21
	$3,11,l$	
−3	18	19
−2	22	21
−1	14	16
0	18	16
1	−13	15
3	−22	21
	$3,12,l$	
−3	16	16
0	−20	22
1	−18	17
	$3,13,l$	
−2	−21	18
1	9	10
	$3,14,l$	
1	11	11
	$4,-15,l$	
0	19	17
	$4,-13,l$	
0	−16	14
	$4,-12,l$	
3	16	17
	$4,-11,l$	
0	10	13
	$4,-10,l$	
0	12	11
2	19	24
3	−13	15
	$4,-9,l$	
−1	15	19
0	−9	10
2	−23	24
3	−18	19
	$4,-8,l$	
0	−34	38
1	−12	12
2	−25	27
3	19	18
	$4,-7,l$	
−3	−25	27
−1	−30	33
0	7	12
3	35	35
	$4,-6,l$	
−2	12	18
0	56	55
1	23	23
2	32	33
3	−16	18
	$4,-5,l$	
−3	31	32
−2	24	26
−1	40	41
0	9	9
1	−21	23
2	−34	32
3	−52	46
	$4,-4,l$	
−2	−21	24
−1	−15	18
0	−71	59
1	−29	29
2	−41	37
3	9	12
	$4,-3,l$	
−3	−62	67
−2	−37	36
−1	−50	45
0	−10	9
1	40	42
2	34	29
3	55	45
	$4,-2,l$	
−6	−25	30
−5	−23	26
−3	−43	44
−2	19	20
−1	36	31
0	85	61
1	52	44
2	18	18
4	−29	35
5	−24	31
6	−20	23
	$4,-1,l$	
−6	−18	23
−5	16	19
−4	21	30
−3	53	45
−2	39	27
−1	48	34
0	17	17
1	−30	27
2	−47	44
3	−63	59
5	−20	24
	$4,0,l$	
−9	−5	10
−8	10	10
−6	23	26
−5	30	32
−4	29	33
−3	17	18
−2	−21	19
−1	−38	27
0	−84	72
1	−34	29
2	−32	35
3	12	14
4	19	20
5	20	21
6	21	19
	$4,1,l$	
−6	15	19

TABLE 3. (*Continued.*)

l	F_c	$\lvert F_o \rvert$
−5	−12	14
−2	−61	46
−1	−39	29
0	−11	13
1	55	43
2	25	23
3	49	42
4	12	13
5	14	14
	4,2,*l*	
−3	−27	25
−2	41	33
−1	20	19
0	77	57
1	31	27
2	25	24
4	−24	24
6	−19	17
	4,3,*l*	
−3	38	28
−2	52	36
−1	19	16
0	11	13
1	−38	32
2	−21	20
3	−31	30
	4,4,*l*	
−3	30	25
−2	−31	26
−1	−26	24
0	−50	43
1	−28	27
	4,5,*l*	
−3	−36	23
−2	−40	33
−1	−14	15
0	−6	10
1	29	28
3	24	23
	4,6,*l*	
−3	−20	19
−2	21	20
−1	20	20
0	29	30
1	17	19
	4,7,*l*	
−3	19	19
−2	28	26
0	12	12
1	−14	17
	4,8,*l*	
0	−15	16
1	−14	14
	4,9,*l*	
−2	−19	18
	4,11,*l*	
0	13	15
	5,−16,*l*	
0	−14	12
	5,−15,*l*	
2	17	15
	5,−14,*l*	
0	24	23
	5,−13,*l*	
−3	27	27
−1	12	13
1	−19	19
2	−18	18
3	−23	22
	5,−12,*l*	
−1	−21	22
0	−36	33
1	−12	13
3	12	14
	5,−11,*l*	
−3	−30	29
−2	−21	21
−1	−13	13
0	9	12
1	22	23
2	26	24
3	25	23
	5,−10,*l*	
−2	25	24
−1	28	30
0	46	40
1	13	15
3	−19	21
	5,−9,*l*	
−3	37	37
−2	21	22
−1	26	27
0	−13	13
1	−34	36
2	−25	25
3	−32	32
	5,−8,*l*	
−2	−40	38
−1	−24	26
0	−49	45
1	−12	13
2	−15	16
	5,−7,*l*	
−3	−48	46
−2	−34	33
0	8	9
1	42	40
2	16	18
	5,−6,*l*	
−2	38	38
−1	32	34
0	39	48
3	−12	14
	5,−5,*l*	
−3	43	42
−2	30	34
1	−37	30
2	−9	14
3	−31	30
	5,−4,*l*	
−2	−42	43
−1	−12	14
0	−40	38
1	−16	16
	5,−3,*l*	
−3	−43	45
−2	−25	24
−1	−5	6
0	13	16
1	21	22
3	24	23
	5,−2,*l*	
−6	−15	19
−5	−33	35
−3	−17	20
−2	36	33
−1	18	18
0	14	13
1	6	9
3	16	18
	5,−1,*l*	
−6	−13	15
−4	13	16
−3	29	31
−2	11	10
0	18	20
1	−19	20
2	16	20
3	−11	16
5	−19	19
	5,0,*l*	
−6	13	15
−5	25	24
−3	13	14
−2	−10	7
0	−9	11
2	−13	12
3	−19	20
5	−13	14
	5,1,*l*	
−2	−17	16
−1	16	16
0	−28	26
2	−25	24
	5,2,*l*	
−3	−19	20
−2	11	13
−1	−16	15
0	−10	12
3	36	32
	5,3,*l*	
0	31	27
1	12	10
2	22	23
	5,4,*l*	
0	16	16
1	−14	12
3	−21	22
	5,5,*l*	
0	−33	30
1	−19	20
2	−29	28
	5,6,*l*	
−3	−19	17
−1	−21	19
0	−20	20
3	30	30
	5,7,*l*	
−3	−17	15
0	27	28
1	25	26
2	14	17
	5,8,*l*	
−3	19	16
−1	21	15
0	10	12
3	−27	24
	5,9,*l*	
0	−22	21
1	−21	22
	5,10,*l*	
0	−15	17
1	11	10
3	17	13
	5,11,*l*	
0	17	18
1	14	15
	5,12,*l*	
0	11	11
	5,13,*l*	
0	−11	9
	6,−10,*l*	
3	18	18
	6,−9,*l*	
0	21	19
2	17	21
	6,−8,*l*	
−1	20	22
2	−19	19
3	−21	20
	6,−7,*l*	
0	−36	31
2	−24	26
	6,−6,*l*	
−3	−25	24
−1	−30	34
2	28	27
3	28	29
	6,−5,*l*	
−3	−11	16
0	49	43
1	31	33
2	19	20
	6,−4,*l*	
−3	34	37
−2	21	26
−1	31	33
0	13	14
1	−22	24
2	−20	23
3	−46	39
	6,−3,*l*	
−3	17	18
−2	−15	16
−1	−25	26
0	−44	38
1	−35	31
2	−31	28
	6,−2,*l*	
−3	−39	36
−2	−36	33
−1	−41	40
1	29	33
2	21	21
3	46	44
	6,−1,*l*	
−6	−14	17
−5	−23	24
−4	−19	23
−3	−22	22
−2	20	19
−1	17	22
0	63	54
1	32	30
2	20	22
4	−20	21
5	−13	14
6	−16	16
	6,0,*l*	
−7	−10	13
−6	−15	17
−5	14	14
−4	9	11
−3	43	39
−2	38	30
−1	23	24
0	16	17
1	−33	32
2	−18	18
3	−40	37
4	−9	10
5	−13	11
	6,1,*l*	
−2	−22	22
−1	−23	24
0	−55	47
1	−29	27
4	17	16
	6,2,*l*	
−3	−33	34
−2	−44	38
−1	−18	21
0	−16	17
1	31	32
2	23	23
3	24	21
	6,3,*l*	
0	41	40
1	18	18
2	17	18
	6,4,*l*	
0	14	11
1	−24	26
	6,5,*l*	
0	−26	27
1	−16	18
	6,6,*l*	
1	9	12
	6,7,*l*	
0	13	15
	7,−14,*l*	
1	15	13
	7,−13,*l*	
0	22	18
	7,−12,*l*	
−3	22	22
1	−17	17
2	−18	17
3	−22	17
	7,−11,*l*	
−1	−15	15
0	−36	28
	7,−10,*l*	
−3	−33	27
−1	−16	17
1	26	24
3	26	23
	7,−9,*l*	
−2	24	26
−1	22	23
0	42	33
1	13	13
	7,−8,*l*	
−3	37	42
−2	19	20
1	−22	22
2	−26	25
3	−17	16
	7,−7,*l*	
−2	−23	29
−1	−20	21
0	−38	33
	7,−6,*l*	
−3	−33	36
−2	−34	36
1	30	27
3	16	18
	7,−5,*l*	
−2	29	32
−1	24	27
0	30	29
	7,−4,*l*	
−3	23	28
−2	21	25
1	−22	23
3	−17	19
	7,−3,*l*	
−2	−25	29
0	−24	23
1	−10	10
	7,−2,*l*	
−4	−13	16
−3	−17	21
−2	−25	24
1	13	17
2	−9	12
	7,−1,*l*	
−5	−27	25
−3	−13	16
−2	22	23
3	20	20
	7,0,*l*	
−8	−15	12
−7	−9	9
−3	9	10
−2	16	14
−1	−9	11
0	19	18
2	8	14
5	−13	11
6	−10	8
	7,1,*l*	
−1	11	15
3	−14	14
	7,2,*l*	
1	−13	15
2	−15	17
	7,3,*l*	
0	−14	14
3	21	19
	7,4,*l*	
0	23	23
2	17	20
	7,5,*l*	
0	12	16
3	−19	18
	7,6,*l*	
0	−20	21
1	−15	14
	7,7,*l*	
0	−14	14
3	15	16
	7,8,*l*	
0	17	19
1	15	17
	7,10,*l*	
0	−11	8
	8,−9,*l*	
3	17	14
	8,−7,*l*	
3	−21	21
	8,−6,*l*	
0	−29	28
1	−8	11
2	−19	23
	8,−5,*l*	
−1	−17	15
0	−9	12
1	11	12
2	15	16
3	28	27
	8,−4,*l*	
0	40	39
1	16	19
2	18	20
	8,−3,*l*	
−3	27	31
0	11	14
1	−23	22
3	−21	23
	8,−2,*l*	
−6	14	17
−5	15	16
−3	20	23
−2	−20	22
0	−42	41
1	−17	19
2	−18	23
4	12	15
	8,−1,*l*	
−3	−26	26
−2	−26	28
−1	−21	24
0	−11	15
1	15	18

TABLE 3. (*Continued.*)

l	F_c	$\lvert F_o \rvert$
2	22	25
3	26	24
	8,0,l	
−6	−8	11
−5	−20	23
−4	−10	12
−3	−20	21
−2	18	18
−1	9	10
0	31	30
1	31	30
4	−8	11
	8,1,l	
−2	24	27
−1	22	23
1	−10	13
3	−24	23
	8,2,l	
−3	17	21
−1	−19	23
0	−24	22
1	−18	20
	8,3,l	
0	−12	13
1	18	18
	8,4,l	
0	20	19
1	13	13
	8,5,l	
0	11	11
1	−13	14
	8,6,l	
0	−10	11
	9,−12,l	
0	22	19
	9,−11,l	
1	−19	17
	9,−10,l	
0	−17	11
1	−15	15
	9,−9,l	
−3	−22	20
1	15	16
	9,−8,l	
0	29	28
	9,−7,l	
−3	23	25
1	−19	21
	9,−6,l	
0	25	27
	9,−5,l	
−3	24	27
1	20	20
	9,−4,l	
0	18	15
	9,−3,l	
1	13	19
	9,−2,l	
−5	17	19
−2	13	17
	9,−1,l	
−2	16	16
	9,0,l	
−5	14	15
−3	9	11
−2	6	10
3	13	12
	9,3,l	
0	15	13
	9,5,l	
0	13	13
	10,−7,l	
0	18	15
	10,−5,l	
0	−21	20
	10,−3,l	
0	21	21
1	14	16
	10,−2,l	
−3	13	17
−2	21	22
1	−12	11
3	−16	17
	10,−1,l	
−3	10	15
−1	13	15
0	19	20
1	13	16
	10,0,l	
−3	12	13
−2	15	17
−1	−11	13
0	−11	11
1	14	13
2	8	9
3	13	14
	10,1,l	
0	20	21
1	12	12
	10,3,l	
0	−12	13
	10,5,l	
0	8	9
1	7	9
	11,−1,l	
−5	11	13
	12,−2,l	
0	11	14
	12,0,l	
−5	8	9
−3	8	10
0	−11	12
1	−8	8

Intensity data were collected from equi-inclination Weissenberg photographs of the layers $hk0 \longrightarrow hk3$, $0kl \longrightarrow 2kl$, and $h0l \longrightarrow h2l$ by the multiple-film technique. The intensities were measured visually; Lorentz and polarisation factors were obtained from a Cochran chart.[3] No allowance was made for absorption or extinction. The structure amplitudes were placed on a common arbitrary scale by internal correlation; 1280 of a possible 2850 independent reflections were obtained.

Approximate positions for copper and iodine atoms were obtained from a three-dimensional Patterson map. Using an overall temperature factor with $B = 3{\cdot}0$ Å^2 and these co-ordinates [I(1) 0·370, 0·270, 0·120; I(2) 0·870, 0·230, 0·080; Cu 0·870, 0·230, 0·440] led to calculated structure factors with a discrepancy factor (R) of 0·30. The remaining atoms (excluding hydrogen) were located in a three-dimensional electron-density distribution and a difference Fourier with copper and iodine atoms removed.

The scattering factors of Thomas and Umeda [4] for iodine and Berghuis *et al.*[5] for copper, carbon, and nitrogen were used. Dispersion corrections [6] were applied to the scattering curves of iodine and copper.

Calculations were carried out on UTECOM (a Deuce electronic digital computer) with programmes written by Dr. J. S. Rollett.[7]

The trial structure was refined by successive Fourier and structure factor calculations to the limiting value of $R = 0{\cdot}18$. Further refinement was carried out by a least-squares procedure in which $\sum w(|F_o| - |F_c|)^2$ was minimised. Anistropic temperature parameters were included in the refinement. Two cycles of refinement giving equal weights to all reflections caused a fall in R to 0·15. The weighting scheme was then changed so that the weight, w, assigned to each reflection was: $|F_o| \leqslant 5|F_{\text{min.}}|$, $w = (F_o/5F_{\text{min.}})^2$; $|F_o| > 5|F_{\text{min.}}|$, $w = (5F_{\text{min.}}/F_o)^2$. Owing to the limited storage capacity of the computer, the copper and iodine atoms had to be refined separately from the light atoms by using $\frac{1}{8}$ absolute scale; the light atoms were refined on $\frac{1}{2}$ absolute scale. The programme solved a 3×3 matrix for the co-ordinates, a 6×6 matrix for the thermal parameters for each atom, and a 2×2 matrix for the scale factor. After three cycles of refinement of the copper and iodine atoms the discrepancy factor reduced to 0·12. Four cycles, in which the light atoms were refined, were then carried out (average shifts for the fourth cycle were 0·006 Å) and, finally, a cycle on the reduced scale was calculated to see if the heavy atom positions were influenced by movements of the light atoms. However, the shifts in the heavy atoms were only 0·001 Å.

[3] Cochran, *J. Sci. Inst.*, 1948, **25**, 253.

[4] Thomas and Umeda, *J. Chem. Phys.*, 1957, **26**, 293.

[5] Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

[6] Dauben and Templeton, *Acta Cryst.*, 1955, **8**, 841.

[7] Rollett, in "Computing Methods and the Phase Problem in X-ray Crystal Analysis," eds. Pepinsky, Robertson, and Speakman, Pergammon Press, New York, 1960.

The final atomic co-ordinates are listed in Table 1; the parameters of the temperature-factor expression,

$$T = 2^{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{23}kl + b_{31}hl + b_{12}hk)},$$

are given in Table 2. The observed structure amplitudes and the final calculated structure factors (discrepancy factor, R = 0·09) are listed in Table 3.

DESCRIPTION OF STRUCTURE

The crystals are composed of iodobis-(2,2′-bipyridyl)copper(II) ions and iodide ions. The copper atoms are covalently bonded to four nitrogen atoms and an iodine atom to form a somewhat distorted, trigonal bipyramid. The arrangement of these ions is shown in Figs. 1(a and b). There are continuous columns of the complex ions parallel to the *c* axis; the copper atoms of adjacent ions are separated by *c*. The copper–iodine bond and the " trigonal " plane of the complex ion are almost parallel to the *c* axis. Each of the columns of complex ions is surrounded by two rows of iodide ions and two other columns of the complex ions [see Fig. 1(b)]. Each complex ion is in contact with four iodide ions and seven other cations, two of which are above and below it in the same column. Each iodide ion has six different complex ions at normal van der Waal's distances. The relevant interionic distances are listed in Table 4.

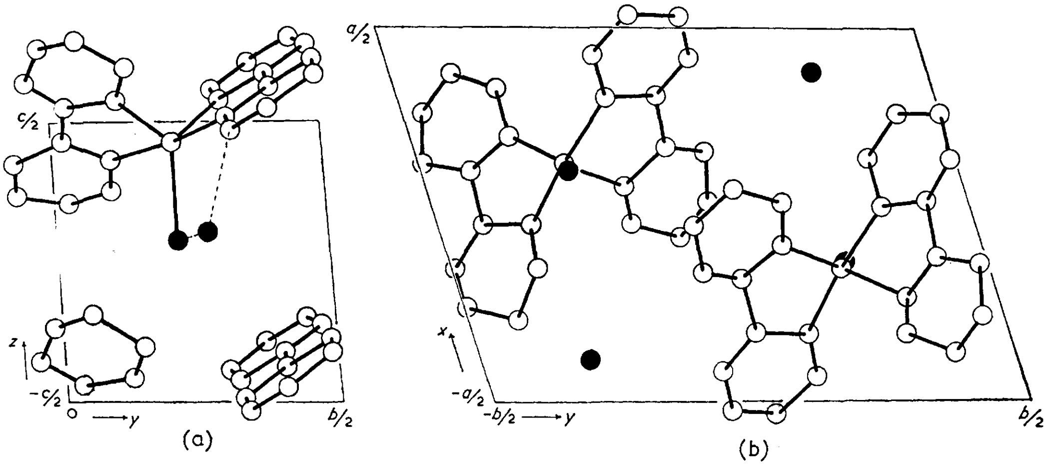

FIG. 1. Atomic arrangement in the unit cell of iodobis-(2,2′-bipyridylcopper(II) iodide: projection on (a) the (100) plane and (b) the (001) plane.

TABLE 4.

Interionic distances.*

Contact	Distance (Å)	Contact	Distance (Å)	Contact	Distance (Å)	Contact	Distance (Å)
I(1)–C(11)	4·10	I(2)–C(16a)	4·07	C(12)–C(17d)	3·36	C(1)–C(3e)	3·70
I(1)–C(12)	4·20	I(2)–C(20a)	4·16	C(12)–C(18d)	3·39	C(2)–C(2e)	3·36
I(1)–C(9a)	4·06	I(2)–C(8b)	4·18	N(4)–C(13d)	3·44	C(2)–C(3e)	3·51
I(1)–C(10a)	4·15	N(2)–C(8b)	3·56	N(4)–C(14d)	3·60	I(2)–C(3f)	4·01
I(1)–C(7b)	4·18	C(6)–C(8b)	3·60	C(13)–C(16d)	3·36	C(1)–C(4f)	3·58
I(1)–C(1c)	3·74	C(6)–C(9b)	3·56	C(13)–C(17d)	3·55	C(2)–C(4f)	3·52
I(1)–C(2c)	4·06	C(7)–C(9b)	3·68	C(13)–C(20d)	3·60	C(2)–C(5f)	3·54
I(1)–C(18d)	4·16	C(7)–C(10b)	3·53	C(14)–C(15d)	3·57	C(2)–C(7f)	3·71
I(2)–N(2a)	4·06	N(3)–C(17d)	3·62	C(14)–C(16d)	3·34	C(3)–C(5f)	3·52
I(2)–N(4a)	3·98	C(11)–C(17d)	3·34	C(15)–C(15d)	3·44	C(3)–C(20f)	3·69
I(2)–C(10a)	3·95	C(11)–C(18d)	3·75	C(16)–C(16d)	3·55		

* The co-ordinates of the atoms marked a—f are related to those in Table 1 as follows:

a, $(x, y, z - 1)$; b, $(\bar{x}, \bar{y}, 1 - z)$; c, $(1 + x, y, z)$; d, $(\bar{x}, 1 - y, 1 - z)$; e, $(\overline{1 + x}, \bar{y}, \bar{z})$; f, $(\overline{1 + x}, \bar{y}, 1 - z)$.

The bond distances and angles in the complex ion are shown in Figs. 2(a and b). The copper–nitrogen bonds vary from 1·96 to 2·10 Å, with an average value of 2·02 Å and a standard deviation of about 0·04 Å; the difference between the two extreme values is therefore not significance. These distances suggest covalent bonding since they compare favourably with previously reported values for copper–nitrogen covalent bonds.[8] No value has been reported for the copper(II)–iodine covalent bond distance. The value found in this case (2·70 Å) is consistent with the sum of the covalent radii for the copper(II) and iodine atoms (1·33 + 1·36 = 2·68 Å) and suggests a normal covalent copper–iodine bond.

The copper atom and the atoms I(2), N(2), and N(4) lie in a plane: the equation for the least-squares plane through these atoms is $0{\cdot}8940X + 0{\cdot}3585Y + 0{\cdot}2688Z - 0{\cdot}2039 = 0$ and the deviations of the atoms from this plane are: Cu, 0·004; I(2), 0·001; N(2), 0·001; N(4), 0·001 Å. The angles formed by the two nitrogen atoms of each 2,2′-bipyridyl molecule with the copper atom are significantly less than 90° (average value 82°, e.s.d. 1·5°); this is probably due to steric requirements of the bipyridyl system. This causes the trigonal-bipyramidal co-ordination polyhedron to be distorted; the line containing the N(1), N(3), and Cu atoms makes an angle of 9° with the normal to the trigonal plane.

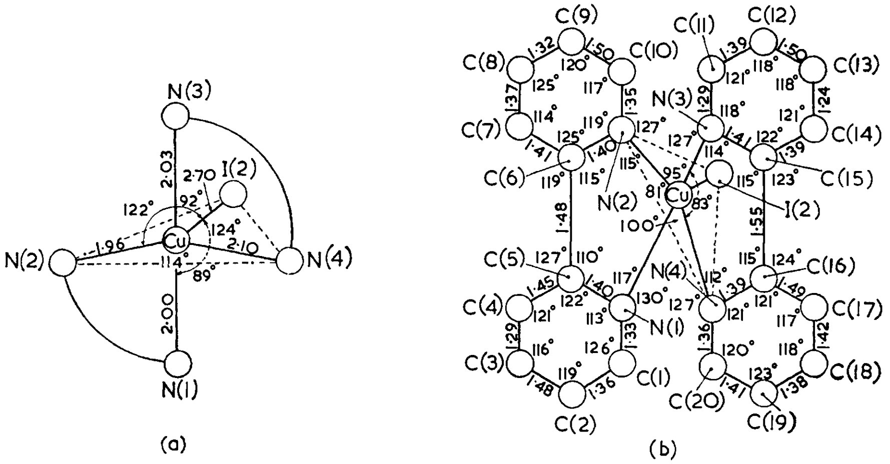

FIG. 2. Bond distances (Å) and bond angles in the iodobis-(2,2′-bipyridyl)copper(II) ion.

The positions of the light atoms are much less accurately determined (average e.s.d. = 0·046 Å) than those of the copper and iodine atoms (average e.s.d. = 0·005 Å). Hence, it is not surprising that there are considerable variations in the determined bond lengths and angles within the bipyridyl ring systems. The carbon–carbon bonds vary from 1·24 to 1·50 Å and the bond angles range from 114° to 126°. These differences are not significant. The average values (C–N 1·36; C–C 1·40 Å; ∠CNC 118°; ∠NCC 122°; ∠CCC 119°) are in good agreement with the values determined for 2,2′-dipyridyl itself[9] (C–N 1·36; C–C 1·39 Å; ∠CNC 117°; ∠NCC 123°; ∠CCC 119°). The average value for the carbon–carbon distance between the two heterocyclic rings in each molecule (1·52 Å) is to be compared with 1·50 Å found between the same carbon atoms in 2,2′-dipyridyl.

Each of the pyridine rings is planar. The average deviation of the atoms from the relevant plane is only about half the estimated standard deviation of their positions. The ligand molecule represented by the atoms N(3), N(4), and C(11)—C(20) is planar since the dihedral angle between the planes of the two pyridine rings (about 2°) cannot be regarded as significant. The dihedral angle between these planes in the other 2,2′-bipyridyl molecule is 10° and could

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[8] Sutton *et al.*, "Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ.*, No. 11, London, 1958.

[9] Merritt and Schroeder, *Acta Cryst.*, 1956, **9**, 801.

be significant. However, the average deviation from the mean plane through all twelve atoms (0·087 Å) does not appear to be significant.

DISCUSSION

The conductivity and magnetic moment for iodobis-(2,2′-bipyridyl)copper(II) iodide are consistent with a structure containing a five-covalent cation. However, it is not necessary for the trigonal-bipyramidal co-ordination of the copper atom to persist in solution since a molecule of solvent could co-ordinate with the copper atom and change the complex ion to give an octahedral stereochemistry.

The trigonal-bipyramidal structure is unusual for copper(II) complexes. Dichloro-2,2′,2″-terpyridylcopper(II) dihydrate is said to have this structure.[10] The more usual structure found for copper(II) compounds is a planar arrangement of four atoms at normal covalent distances from the copper atom, with a fifth and sometimes a sixth atom at longer distances perpendicular to this plane. There does not appear to be any elongation of the bonds in the trigonal-bipyramidal complex ion. This is in keeping with the absence of a degenerate set of orbitals containing an unsymmetrical group of electrons in the trigonal-bipyramidal ligand-field splittings of the copper(II) ions.[11]

Although the factors leading to the trigonal-bipyramidal stereochemistry in the iodobis-(2,2′-bipyridyl)copper(II) ion are not clear, it is likely that steric factors are important. Molecular models and scale drawings indicate that there would be severe steric interference between the hydrogen atoms on 3- and 3′-carbon atoms of the two bipyridyl molecules in a square-planar arrangement. In the structure found, this strain is not present owing to rotation of the two bipyridyl molecules relative to each other. The trigonal-bipyramidal configuration would result from an extreme distortion of a square-pyramidal arrangement, *viz.*, two *trans*-ligand atoms are moved in a plane containing them, the copper atom, and the fifth ligand atom at the apex of the square pyramid to a position in which the angles made by these atoms with the copper atom and the fifth ligand atom are 120°. Before this stereochemistry can be adopted by a metal, suitable bonding orbitals must be available. This configuration is predicted when ns,np^3,nd bonding orbitals are used.[12]

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[10] Corbridge and Cox, *J.*, 1956, 594.

[11] Lewis and Wilkins, " Modern Co-ordination Chemistry," Interscience Publ., Inc., New York, 1960, p. 442.

[12] Kimball, *J. Chem. Phys.*, 1940, **8**, 188; Daudel and Bucher, *J. Chim. phys.*, 1945, **42**, 6.