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Structure of Bis(2,2′-bipyridine)tris(ethyl isocyanide)molybdenum(II) Bis(tetrafluoroborate), $[Mo(C_2H_5NC)_3(C_{10}H_8N_2)_2][BF_4]_2$

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(*Received* 1 *June* 1984; *accepted* 2 *October* 1984)

Abstract. $M_r = 747·15$, monoclinic, $P2_1/a$, $a = 14·584\ (5)$, $b = 14·072\ (5)$, $c = 17·281\ (5)$ Å, $\beta = 113·35\ (3)°$, $V = 3256·06$ Å^3, $Z = 4$, $D_x = 1·52$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0·71069$ Å, $\mu = 0·41$ mm^{-1}, $F(000) = 1512$, $T = 253 \pm 1$ K, $R = 0·082$ for 3991 observed reflections. The complex is monomeric with an isocyanide-capped distorted octahedral geometry. The influence of donor atoms *trans* to particular metal–ligand bonds is apparent in three types of Mo—N distances [ave. 2·198 Å, *trans* to nitrogen, 2·211 (10) Å *trans* to carbon, 2·257 (10) Å no *trans* donor ligand] and two types of Mo—C distance [2·096 (14) Å, *trans* to nitrogen, ave. 2·028 Å no *trans* donor ligand]. The isocyanide ligands are significantly distorted (ave. ∠CNC 161°).

Introduction. The preparation of seven-coordinate *cis*-$[Mo(CO)_2(bpy)_2(NCMe)][BF_4]_2$ (bpy is 2,2′-bipyridine) by oxidation of *cis*-$[Mo(CO)_2(bpy)_2]$ with silver(I) tetrafluoroborate in methyl cyanide solution has provided a versatile precursor for the chemistry of molybdenum(II). Reaction of precisely three equivalents of an isocyanide, *R*NC, with the molybdenum(II) salt in methyl cyanide solution produces $[Mo(bpy)_2(CNR)_3][BF_4]_2$ (R = Et, *p*-tolyl) (Connor, James, Overton & El Murr, 1984). No other structures of the class $[M(\text{bidentate ligand})_2(CNR)_3]^{2+}$ have been determined. The X-ray structure of $[Mo(bpy)_2(CNEt)_3][BF_4]_2$ is reported.

Experimental. Deep-purple crystals obtained from acetone/diethyl ether were sealed in glass capillaries under nitrogen for X-ray work. Enraf–Nonius CAD-4 diffractometer, crystal size 0·4 × 0·25 × 0·2 mm, cell dimensions from setting angles for 25 widely distributed reflections, graphite-monochromated Mo $K\alpha$ radiation, empirical absorption correction (North, Phillips & Mathews, 1968), 5690 reflections scanned, $\omega/2\theta$ mode, $2·0 \leq \theta \leq 25·0°$, index range h −17 to 17, k 0 to 16, l 0 to 20, no decay in intensity of three reflections checked every 3600 s exposure time, no slippage in orientation for two reflections checked every 100 measurements, 3991 reflections with $I > 1·5\sigma(I)$ used in analysis. Structure solved by heavy-atom method and refined by full-matrix least squares. Non-hydrogen atoms in the cation were refined anisotropically, atoms in the BF_4^- ions and the ethyl carbons of two EtNC groups which showed very high thermal motion refined isotropically. Only H atoms on the bipyridine groups were included, and these were fixed in idealized positions. To achieve stable refinement, the C_α—C_β and C_α—N bond distances in the EtNC ligands were fixed at 1·50 and 1·45 Å respectively. $\sum w(\Delta F)^2$ minimized, final shifts all $<0·04\sigma$, unit weights, $R = 0·082$, residual electron

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density in final difference map within −0·7 and +0·6 e Å^{-3}. Computations were made with *SHELX76* (Sheldrick, 1976) using complex neutral-atom scattering factors (*International Tables for X-ray Crystallography,* 1974).

Discussion. The final atomic coordinates for the non-hydrogen atoms are listed in Table 1* and selected bond lengths and angles in Table 2. The crystal contains discrete monomeric units. The Mo atom in the cation is seven-coordinate with a distorted capped octahedral geometry, the donors comprising two 2,2′-bipyridine and three ethyl isocyanide ligands. The overall geometry of the cation and the atomic numbering scheme are shown in Fig. 1.

The Mo—N bond lengths are of three types: (*a*) those which are *trans* to nitrogen N(11), N(21), average 2·198 Å; (*b*) N(12), *trans* to isocyanide carbon, 2·211 (10) Å; and (*c*) N(22) which does not interact strongly with either C(1*c*) or C(1*a*), 2·257 (10) Å. These bond lengths can be compared with those in the molybdenum(0) complexes, *cis*-[Mo(CO)$_2$(bpy)$_2$], in

Table 1. *Atom coordinates* (×10^4) *and isotropic temperature factors* (Å^2 ×10^3)

	x	y	z	$U_{\rm iso}$ or $U_{\rm eq}$
Mo(1)	−137 (1)	5307 (1)	2715 (1)	34*
N(11)	629 (6)	5711 (6)	4037 (5)	36*
C(11)	852 (8)	6617 (7)	4290 (7)	43*
C(12)	1403 (8)	6871 (9)	5104 (7)	53*
C(13)	1739 (8)	6169 (9)	5705 (7)	58*
C(14)	1524 (7)	5239 (9)	5466 (6)	52*
C(15)	970 (7)	5013 (7)	4620 (6)	39*
C(16)	744 (7)	4051 (8)	4299 (7)	42*
C(17)	1105 (9)	3241 (8)	4773 (8)	58*
C(18)	908 (11)	2362 (9)	4421 (10)	73*
C(19)	347 (10)	2289 (9)	3566 (11)	66*
C(20)	6 (8)	3111 (8)	3111 (8)	54*
N(12)	196 (6)	3980 (6)	3459 (5)	40*
N(21)	−373 (6)	4748 (6)	1453 (5)	41*
C(21)	−1237 (8)	4756 (9)	781 (7)	54*
C(22)	−1385 (10)	4323 (9)	18 (7)	60*
C(23)	−596 (10)	3860 (10)	−56 (8)	64*
C(24)	319 (10)	3871 (9)	625 (8)	62*
C(25)	419 (8)	4336 (7)	1350 (7)	43*
C(26)	1377 (8)	4456 (8)	2060 (7)	47*
C(27)	2280 (10)	4189 (11)	2019 (9)	74*
C(28)	3160 (9)	4345 (12)	2688 (10)	83*
C(29)	3165 (8)	4745 (12)	3405 (9)	76*
C(30)	2257 (7)	5031 (9)	3417 (7)	59*
N(22)	1373 (6)	4892 (6)	2747 (5)	45*
C(1*a*)	−1524 (8)	4733 (10)	2321 (6)	56*
N(1*a*)	−2307 (8)	4370 (9)	2099 (7)	79*
C(2*a*)	−3378 (10)	4165 (16)	1696 (13)	141 (7)
C(3*a*)	−3385 (24)	3128 (17)	1817 (21)	245 (15)
C(1*b*)	−96 (8)	6555 (8)	2068 (7)	48*
N(1*b*)	−88 (9)	7252 (8)	1709 (8)	76*
C(2*b*)	118 (20)	8247 (12)	1568 (17)	186 (11)
C(3*b*)	−716 (20)	8359 (20)	745 (16)	196 (11)
C(1*c*)	−1096 (8)	6240 (8)	2889 (6)	45*
N(1*c*)	−1611 (7)	6794 (7)	3014 (6)	56*
C(2*c*)	−2216 (10)	7650 (10)	2938 (7)	72*
C(3*c*)	−2448 (11)	8106 (11)	2096 (8)	82*
B(11)	890 (13)	−711 (13)	3899 (12)	79 (4)
F(11)	1562 (8)	−1272 (8)	3745 (7)	140 (4)
F(12)	56 (9)	−1203 (8)	3669 (7)	139 (4)
F(13)	698 (10)	37 (10)	3350 (9)	180 (5)
F(14)	1290 (13)	−350 (13)	4622 (11)	230 (7)
B(21)	3406 (18)	3431 (18)	536 (15)	110 (7)
F(21)	2420 (11)	3163 (10)	241 (9)	179 (5)
F(22)	3387 (9)	4345 (10)	689 (8)	157 (4)
F(23)	3902 (11)	2904 (11)	1188 (9)	183 (5)
F(24)	3690 (10)	3280 (10)	−100 (9)	177 (5)

* $U_{\rm eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33} + 2U_{13}\cos\beta)$.

Table 2. *Selected distances* (Å) *and angles* (°)

N(11)–Mo(1)	2·182 (10)	N(12)–Mo(1)	2·211 (10)
N(21)–Mo(1)	2·213 (10)	N(22)–Mo(1)	2·257 (10)
C(1*a*)–Mo(1)	2·029 (13)	C(1*b*)–Mo(1)	2·096 (14)
C(1*c*)–Mo(1)	2·026 (13)		
C(11)–N(11)	1·345 (13)	C(15)–N(11)	1·353 (12)
C(12)–C(11)	1·362 (15)	C(13)–C(12)	1·376 (17)
C(14)–C(13)	1·371 (17)	C(15)–C(14)	1·397 (14)
C(16)–C(15)	1·450 (15)	C(17)–C(16)	1·380 (15)
N(12)–C(16)	1·355 (13)	C(18)–C(17)	1·358 (19)
C(19)–C(18)	1·380 (20)	C(20)–C(19)	1·378 (18)
N(12)–C(20)	1·342 (14)		
C(21)–N(21)	1·333 (13)	C(25)–C(21)	1·365 (13)
C(22)–C(21)	1·389 (16)	C(23)–C(22)	1·372 (18)
C(24)–C(23)	1·386 (18)	C(25)–C(24)	1·368 (16)
C(26)–C(25)	1·458 (15)	C(27)–C(26)	1·397 (16)
N(22)–C(26)	1·339 (14)	C(28)–C(27)	1·362 (19)
C(29)–C(28)	1·359 (19)	C(30)–C(29)	1·392 (16)
N(22)–C(30)	1·362 (13)		
N(1*a*)–C(1*a*)	1·167 (14)	C(2*a*)–N(1*a*)	1·465 (10)
C(3*a*)–C(2*a*)	1·476 (11)	N(1*b*)–C(1*b*)	1·165 (15)
C(2*b*)–N(1*b*)	1·472 (11)	C(3*b*)–C(2*b*)	1·468 (11)
N(1*c*)–C(1*c*)	1·161 (14)	C(2*c*)–N(1*c*)	1·468 (15)
C(3*c*)–C(2*c*)	1·502 (11)		
N(12)–Mo(1)–N(11)	72·9 (4)	N(21)–Mo(1)–N(11)	159·9 (3)
N(21)–Mo(1)–N(12)	100·7 (4)	N(22)–Mo(1)–N(11)	87·3 (4)
N(22)–Mo(1)–M(12)	77·3 (4)	N(22)–Mo(1)–N(21)	72·6 (4)
C(1*a*)–Mo(1)–N(11)	118·9 (5)	C(1*a*)–Mo(1)–N(12)	79·6 (5)
C(1*a*)–Mo(1)–N(21)	77·5 (5)	C(1*a*)–Mo(1)–N(22)	137·6 (4)
C(1*b*)–Mo(1)–N(11)	103·4 (5)	C(1*b*)–Mo(1)–N(12)	166·6 (3)
C(1*b*)–Mo(1)–N(21)	78·3 (5)	C(1*b*)–Mo(1)–N(22)	89·8 (4)
C(1*b*)–Mo(1)–C(1*a*)	112·9 (5)	C(1*c*)–Mo(1)–N(11)	76·9 (4)
C(1*c*)–Mo(1)–N(12)	117·8 (5)	C(1*c*)–Mo(1)–N(21)	122·0 (4)
C(1*c*)–Mo(1)–N(22)	152·7 (4)	C(1*c*)–Mo(1)–C(1*a*)	69·6 (6)
C(1*c*)–Mo(1)–C(1*b*)	72·8 (5)		
N(1*a*)–C(1*a*)–Mo(1)	177·5 (13)	C(2*a*)–N(1*a*)–C(1*a*)	164·0 (16)
C(3*a*)–C(2*a*)–N(1*a*)	101·1 (19)	N(1*b*)–C(1*b*)–Mo(1)	178·9 (10)
C(2*b*)–N(1*b*)–C(1*b*)	159·4 (17)	C(3*b*)–C(2*b*)–N(1*b*)	96·8 (19)
N(1*c*)–C(1*c*)–Mo(1)	177·1 (10)	C(2*c*)–N(1*c*)–C(1*c*)	160·9 (11)
C(3*c*)–C(2*c*)–N(1*c*)	109·5 (11)		

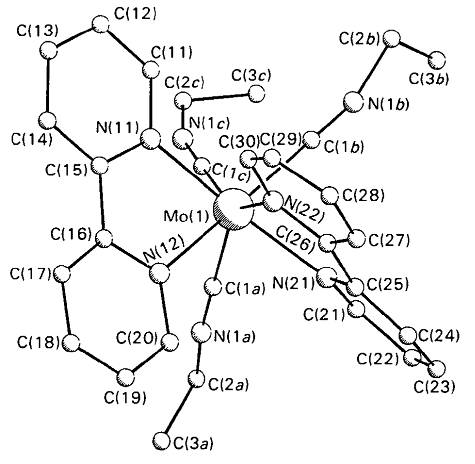

Fig. 1. View of the structure of the [Mo(bpy)$_2$(CNEt)$_3$]$^{2+}$ ion, showing the atomic numbering scheme.

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and additional bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39804 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

which Mo—N *trans* to nitrogen is shorter [2·149 (6) Å], consistent with the change in formal oxidation state, and Mo—N *trans* to the stronger π-acceptor CO ligand is longer [2·230 (6) Å] (Chisholm, Connor, Huffman, Kober & Overton, 1984), and *fac*-$[Mo(CO)_3(bpy)(py)]$ in which Mo—N(bpy) is 2·235 (7) Å (Griffiths, 1971).

The Mo—C distances are of two types: (*a*) C(1*b*) *trans* to nitrogen, N(12), 2·096 (14) Å, which compares with the shortest Mo—C distance in $[Mo(dppm)(CNMe)_5]^{2+}$ [2·090 (9) Å] and in $[Mo(dppe)(CNMe)_5]^{2+}$ [2·096 (7) Å] (Dewan, Wood, Walton & Lippard, 1982);* and (*b*) C(1*a*), C(1*c*) (ave. 2·028 Å) which are among the shortest measured for molybdenum(II)–isocyanide complexes, which typically contain Mo—CN*R* bond lengths in the range 2·04—2·16 Å. The dimensions of the isocyanide ligands in $[Mo(bpy)_2(CNEt)_3]^{2+}$ show two features: (*a*) the C≡N bond is slightly longer (ave. 1·164 Å) than in other molybdenum(II)–isocyanide complexes {*e.g.* 1·14 Å in $[Mo(CNEt)_7]^{2+}$ (Brant, Cotton, Sekutowski, Wood & Walton, 1979), 1·144 Å in $[Mo(dppe)(CNMe)_5]^{2+}$ (Dewan *et al.*, 1982)} consistent with the greater σ-donor strength of two bpy ligands, and (*b*) the CNC angle (ave. 161·0°) is significantly distorted in all three isocyanide ligands from its typical value (177°) in similar structures (Brant *et al.*, 1979; Dewan *et al.*, 1982).

Oxidation has no significant influence on the bpy ligand bite angle {$[Mo(bpy)_2(CNEt)_3]^{2+}$ (ave. 72·7°); *cis*-$[Mo(CO)_2(bpy)_2]$ (ave. 73·6°) (Chisholm *et al.*, 1984)}. Based on bpy ligand dimensions, the average charge on the bpy ligand in $[Mo(bpy)_2(CNEt)_3]^{2+}$ is similar to that in *cis*-$[Mo(CO)_2(bpy)_2]$ (Chisholm *et al.*, 1984) and less than that in $[Mo(OPr^i)_2(bpy)_2]$ (Chisholm, Huffman, Rothwell, Bradley, Kress & Woodruff, 1981).

The absence of both a mirror plane in the cation and a twofold axis passing through Mo—C(1*b*)—N(1*b*), together with the facts that (*a*) the Mo atom is not coplanar with the isocyanide donor atoms C(1*a*), C(1*b*), and C(1*c*), (*b*) there is a large dihedral angle between the planes of the bpy ligands and (*c*) the value of the normalized bite (Kepert, 1979) of the bpy ligand is small ($b = 1·18$), all indicate the low symmetry of the cation. The isocyanide-capped distorted octahedral geometry at molybdenum in this salt is a further example of stereochemistry V (Kepert, 1979) in the $[M(\text{bidentate})_2(\text{unidentate})_3]^{x\pm}$ series.

We thank the SERC for a Studentship (CO) and for support of the crystallographic facility at Queen Mary College (JAC).

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* dppm is bis(diphenylphosphino)methane, dppe is 1,2-bis(diphenylphosphino)ethane.

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Acta Cryst. (1985). C**41**, 186–189

catena-Tri-μ-chloro-bis(2,6-dimethyl-4-pyrone)lanthanum(III), $[LaCl_3(C_7H_8O_2)_2]_n$

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(*Received* 27 *July* 1984; *accepted* 1 *October* 1984)

Abstract. $M_r = 493·55$, monoclinic, $P2_1$ or disordered $P2_1/m$, $a = 11·202\ (7)$, $b = 7·944\ (1)$, $c = 10·011\ (6)$ Å, $\beta = 102·55\ (7)°$, $V = 869·6\ (5)$ Å^3, $Z = 2$, $D_x = 1·885$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu = 29·7$ cm^{-1}, $F(000) = 480$, $T = 293$ K. Final $R = 3·5\%$ for 1697 unique observed reflections. Each La^{III}

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