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1,10-Phenanthroline Substitution in *Trans*-Dioxotetracyanomolybdate(IV)ions. The Crystal Structure of $Na[MoO(CN)_3(Phen)]\cdot 2Phen\cdot CH_3OH\cdot H_2O$

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The crystal structure of $Na[MoO(CN)_3(phen)]\cdot 2phen\cdot CH_3OH\cdot H_2O$ *was determined from three-dimensional X-ray data. The brown-black crystals are monoclinic, space group* $P2_1/c$, *with cell dimensions* $a = 15.090$, $b = 14.584$, $c = 18.126$ Å, $\beta = 111.55°$ *and containing four molecules per unit cell. The structure was solved from 3655 observed reflections. The anisotropic refinement converged to* $R = 0.075$.

The $[MoO(CN)_3(phen)]^-$ *ion is a distorted octahedron with the oxygen and a cyanide ligand* trans-*orientated to the bidentate ligand atoms. The two Mo–N bonds (2.173(8) and 2.363(7) Å) differ significantly with the longer one* trans *to the strong Mo=O = 1.669(8) Å bond. The cyanide ligands have two normal* $Mo–C_{av} = 2.15(1)$ *Å bond distances and a significantly shorter Mo–C = 2.09(1) Å bond* trans *to the shorter Mo–N bond. The distorted six-atom environment of each sodium ion originates from one methanol, one water and two phenanthroline molecules.*

Introduction

It is well-known [1] that the *trans*-dioxotetracyanomolybdate(IV)ion can be protonated in alkaline solution according to reactions (1) and (2).

$$MoO_2(CN)_4{}^{4-} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} MoO(OH)(CN)_4{}^{3-} \qquad (1)$$

$$MoO(OH)(CN)_4{}^{3-} \underset{-H^+}{\overset{+H^+}{\rightleftharpoons}} MoO(H_2O)(CN)_4{}^{2-} \qquad (2)$$

The existence of these ionic species was further confirmed by crystal structure determinations on $NaK_3[MoO_2(CN)_4]\cdot 6H_2O$ [2], $[Cr(en)_3][MoO(OH)(CN)_4]\cdot H_2O$, $[Pt(en)_2][MoO(H_2O)(CN)_4]\cdot 2H_2O$ [3] and $(Ph_4P)_2[MoO(H_2O)(CN)_4]\cdot 4H_2O$ [4]. These results showed that the Mo–O bond lengths gave the expected increase with successive protonation of the oxo ligand. This labilization of the hydroxo but especially the aquo ligand recently led to the isolation and structure determination of $Na[MoO(CN)_3(phen)]\cdot 2phen$ [5], which confirmed the exact nature of the complex ion resulting from a bidentate ligand's reaction with the $MoO_2(CN)_4{}^{4-}$ ion in weakly alkaline solutions.

It was quite often found that the green crystals of the above compound also crystallized in admixture with brown-black crystals which had a tendency to partly dehydrate within a few days. This paper reports the most favourable preparative method and structure determination of this compound in order to identify this alternative product of the phen–$MoO_2(CN)_4{}^{4-}$ reaction.

Experimental

$K_4[Mo(CN)_8]\cdot 2H_2O$ and $NaK_3[MoO_2(CN)_4]\cdot 6H_2O$ was prepared as reported previously [5]. The phen complex was prepared as follows: 0.4 g (0.002 mol) of 1,10-phenanthroline monohydrate was dissolved in 10 cm^3 MeOH and diluted with 40 cm^3 0.075 *M* $NaHCO_3$. To this solution was added 0.48 g (0.001 mol) $NaK_3[MoO_2(CN)_4]\cdot 6H_2O$, stirred until completely dissolved. The dark green solution was covered tightly with a transparent film and stored for *ca.* 3 days, after which brown-black crystals (53% yield) were collected.

Crystal data: $C_{40}H_{30}N_9O_3NaMo$, molecular weight = 803.6, monoclinic space group $P2_1/c$, $a = 15.090$, $b = 14.584$, $c = 18.126$ Å, $\beta = 111.55°$, $Z = 4$, $\mu(Mo\text{-}K_\alpha) = 4.45$ cm^{-1}, measured density = 1.54 g cm^{-3}. Three-dimensional intensity data were collected for θ-values between 3 and 23° on a Philips PW1100 four circle single crystal X-ray diffractometer using graphite monochromated MoK_α radiation ($\lambda = 0.7107$ Å). A crystal with dimensions 0.28 × 0.28 × 0.13 mm, covered with Canada balsam was used for the data collection. No decomposition was detectable during the data collection. A total of 5368 independent reflections were measured, of which 3655 were considered as observed, $I \geqslant 3\sigma(I)$. Only Lorenz and polarization corrections were applied.

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The Mo position was determined by the heavy-atom method and those of other non-hydrogen atoms from subsequent Fourier or difference maps. The final *R* of 0.075 was obtained by a 9-cycle full-matrix least-squares refinement using anisotropic thermal parameters for all non-hydrogen atoms. Atomic scattering factors (interpolated for Mo(IV)) were those tabulated by Cromer and Waber [6]. Calculations were performed with the X-ray 72 system of programs [7]. Final atomic co-ordinates are listed in Table I. A list of the observed and calculated structure factors may be obtained from the authors.

Results and Discussion

A projection of the structure along the *c* axis is presented in Fig. 1. The packing consists of chain-like arrays of alternate cations and anions along [100]. The water and methanol molecules form part of the chain since each couple a cation with an anion. Each complex anion is thus hydrogen bonded through the *trans*-orientated cyanide ligands to a water molecule (O(3)–N(37) = 2.73(2) Å) and a methanol molecule (O(2′)–N(38) = 2.81(1) Å). The latter oxygen atoms are also strongly ion–dipole bonded to separate symmetry related sodium ions at 2.413(9) and 2.38(1) Å for O(2′) and O(3) respectively. The above-mentioned bond data correlate well with those found in for ex. $NaK_3[MoO_2(CN)_4]\cdot 6H_2O$ [2] and $Na_3[W(CN)_8]\cdot 4H_2O$ [8].

Each sodium ion coordinates to two oxygen atoms (one each from a water and methanol molecule) and four nitrogen atoms, the latter belonging to the two phen ligands. The Na–O and Na–N bond distances (Fig. 2) are not sufficiently different to explain the marked departure from regular octahedral or trigonal prismatic geometries in the six-atom environment of each sodium ion. The O–O, O–N and non-chelating N–N distances are also comfortably longer than the expected van der Waals distances for these atoms [9]. The most obvious explanation for distortion in this case is the fixed N–N bite distances (2.76(1) and 2.72(1) Å) of the phen ligands, which as can be seen from Fig. 2, are considerably shorter in comparison to the remaining interatomic distances. Calculations based on the dihedral (δ) and twist angle (ϕ) criteria [10] for distinguishing between the octahedral (D_{3d}) and trigonal prismatic (D_{3h}) forms slightly favour the latter form. The shaded triangle in Fig. 2 thus has a $\phi = 12.9^\circ$ compared to a theoretical zero twist for the D_{3h} and 60° for the D_{3d} forms. The averaged δ-values for the three different sets were calculated as 39, 76 and 96° compared to the theoretical 0, 90 and 120° for D_{3h} and 70.5° of the D_{3d} forms. This indicates a distortion to about half-way between the two idealized models.

It is interesting to compare this result with the more ordered trigonal prismatic environment of sodium ions in $Na[MoO(CN)_3(phen)]\cdot 2phen$ [5]. The packing of the present structure necessitates the inclusion of two different solvent molecules, both bonded to the sodium ion, instead of two nitrogen atoms of cyanide ligands for the latter formulation. The sodium ions in both compounds coordinate two phen ligands in a different way. In $Na[MoO(CN)_3(phen)]\cdot 2phen$ they span the edge of a trigonal and prism plane respectively, whilst in the present case only edges of the prism planes are involved. It is thus expected that with the N(5)–N(6) and N(3)–N(4) edges being shorter than the O(2)–O(3) edge (Fig. 2) this would lead to a considerable tilt of the triangular planes towards one another. On the contrary, these planes form an angle of 9.4° which is still smaller than the 14.5° found in $Na[MoO(CN)_3(phen)]\cdot 2phen$. The main difference between these two sodium ion environments is to be found in the δ-values related to the prism planes alone (0 and 120° theoretically) and this again is mainly the result of a larger twist angle compared to a $\phi = 0^\circ$ calculated for $Na[MoO(CN)_3(phen)]\cdot 2phen$.

The $[MoO(CN)_3(phen)]^-$ ion has a distorted octahedral structure with bonding characteristics (Table II) very similar to those of $Na[MoO(CN)_3(phen)]\cdot 2phen$ [5]. The atom labelling for the complex anion is the same for both compounds, allowing direct comparison of relevant bond data. The distortion follows the previously observed pattern, in that the Mo atom is displaced by 0.39 Å out of the N(1), C(37), C(39) and C(38) plane towards the oxygen atom. This results in smaller than usual contacts between N(2) (*trans* to O(1)) and the cyano carbon atoms. Pertinent data (Table III) are those of C(38)–C(39), C(38)–N(2), C(37)–N(2) and C(37)–C(39) all of which are *ca.* 0.2 Å shorter than the expected values employing van der Waals radii [5]. The same conclusion is also reached in applying theoretical results for the minimization of repulsion energies [11].

Following the application of these results to the case of $Na[MoO(CN)_3(phen)]\cdot 2phen$, we calculated the normalized bite b = 1.17 and angular coordinates $\phi_C = 82.2^\circ$ (for C(38)), 82.1° (for C(37)) and ϕ_E = 132.8° (for O(1)) and 123.0° (for C(39)). For the latter fixed normalized bite the theory predicts minimum repulsion energies at approximate ϕ_C and ϕ_E values of 92 and 132° respectively. With the exception of oxygen all other angular coordinates of the carbon atoms differ by at least 9° (compared to 6° for $Na[MoO(CN)_3(phen)]\cdot 2phen$) from the theoretical values, again indicative of non-bonded repulsions operative on these atoms.

The bond data (Table II) of the phen ligand in the $[MoO(CN)_3(phen)]^-$ ion as well as those of the remaining phen molecules (omitted for space conser-

TABLE I. Fractional Atomic Co-ordinates ($\times 10^4$) and Thermal Parameters ($\times 10^3$) with Estimated Standard Deviations in Parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	4941.2(6)	2050.5(6)	2104.4(5)	42.7(5)	49.1(6)	36.3(6)	−1.9(5)	18.0(4)	−9.8(5)
C(1)	4434(7)	3509(8)	749(7)	42(6)	61(8)	74(8)	−1(5)	30(6)	12(6)
C(2)	4154(9)	3848(9)	−33(8)	73(8)	65(8)	67(8)	−2(7)	32(7)	19(7)
C(3)	3893(9)	3253(9)	−671(7)	64(8)	67(8)	67(8)	−4(6)	30(7)	11(7)
C(4)	3584(7)	1647(9)	−1159(6)	36(6)	84(9)	31(6)	−2(6)	7(5)	0(6)
C(5)	3543(7)	733(8)	−1003(6)	39(6)	69(8)	47(7)	−4(6)	12(5)	4(6)
C(6)	3804(7)	−512(7)	−1(6)	39(6)	62(7)	47(6)	1(5)	19(5)	−2(5)
C(7)	4107(7)	−773(8)	789(7)	45(6)	55(7)	59(7)	−0(7)	20(6)	−0(6)
C(8)	4442(7)	−88(7)	1377(6)	37(6)	48(6)	47(6)	4(5)	20(5)	1(5)
C(9)	4143(6)	1054(7)	429(5)	25(5)	50(7)	38(5)	−1(4)	10(4)	−7(5)
C(10)	4163(6)	1999(7)	262(5)	31(5)	56(6)	31(5)	3(5)	12(4)	−1(5)
C(11)	3869(7)	2311(8)	−529(6)	40(6)	68(8)	38(6)	−2(5)	14(5)	11(5)
C(12)	3828(7)	412(7)	−202(6)	35(6)	53(7)	48(6)	−1(5)	19(5)	2(5)
C(13)	1161(8)	2910(9)	3730(7)	49(7)	67(8)	74(8)	−15(6)	17(6)	3(7)
C(14)	1403(10)	3081(9)	4564(8)	84(9)	65(9)	72(9)	−29(8)	25(7)	−2(7)
C(15)	751(10)	3490(9)	4809(7)	99(11)	63(9)	62(8)	−31(8)	27(8)	−1(7)
C(16)	−863(12)	4225(10)	4449(9)	106(12)	73(9)	83(10)	−11(9)	58(9)	−9(8)
C(17)	−1704(11)	4468(9)	3895(9)	95(11)	61(8)	113(12)	−14(8)	73(10)	−26(8)
C(18)	−2806(9)	4509(8)	2470(9)	78(9)	47(7)	129(12)	−0(7)	61(9)	6(7)
C(19)	−2979(9)	4264(9)	1690(9)	69(9)	62(8)	128(12)	7(7)	52(9)	24(8)
C(20)	−2237(8)	3831(8)	1518(7)	54(7)	62(8)	85(9)	12(6)	25(6)	20(7)
C(21)	−1233(8)	3823(7)	2829(7)	58(7)	43(6)	64(7)	−3(6)	35(6)	6(5)
C(22)	−333(8)	3566(7)	3416(7)	72(8)	48(7)	59(7)	−22(6)	42(6)	−10(6)
C(23)	−145(9)	3751(8)	4233(7)	89(9)	45(7)	72(8)	−25(6)	41(7)	−7(6)
C(24)	−1919(9)	4264(7)	3064(8)	86(9)	42(7)	90(9)	4(6)	63(8)	2(6)
C(25)	1766(8)	3924(8)	1871(7)	52(7)	51(7)	65(8)	−2(6)	9(6)	−5(6)
C(26)	2472(9)	4383(9)	1644(8)	59(8)	64(8)	88(10)	−1(6)	20(7)	−5(7)
C(27)	2245(9)	4535(8)	853(8)	64(8)	49(7)	95(10)	−7(6)	41(7)	−10(7)
C(28)	1087(11)	4444(9)	−551(8)	111(12)	55(8)	73(9)	20(8)	49(9)	9(7)
C(29)	233(11)	4174(9)	−1058(7)	109(11)	61(8)	55(8)	27(8)	40(8)	16(6)
C(30)	−1353(10)	3430(9)	−1317(7)	80(9)	61(8)	47(7)	28(7)	2(7)	−3(6)
C(31)	−1966(9)	3006(10)	−1033(7)	65(8)	77(9)	59(8)	18(8)	−3(6)	−25(7)
C(32)	−1651(8)	2823(9)	−203(7)	67(8)	72(9)	56(7)	13(7)	13(6)	−12(7)
C(33)	−203(8)	3523(7)	24(6)	58(7)	53(7)	34(6)	18(5)	17(5)	−2(5)
C(34)	716(7)	3808(7)	7(6)	58(7)	45(6)	34(6)	10(5)	20(5)	3(5)
C(35)	1352(8)	4261(7)	285(7)	69(8)	41(6)	69(8)	10(6)	39(6)	3(5)
C(36)	−450(9)	3703(8)	−800(6)	87(9)	52(7)	48(7)	28(7)	21(6)	4(6)
C(37)	3480(7)	1882(7)	1989(6)	50(6)	44(7)	53(6)	11(5)	23(5)	0(5)
C(38)	6257(6)	1720(7)	1960(5)	31(5)	56(6)	34(5)	−10(5)	7(4)	−9(5)
C(39)	5286(8)	1117(8)	3042(6)	65(8)	58(7)	54(7)	10(6)	33(6)	3(6)
C(40)	−1213(9)	517(9)	1496(8)	77(9)	70(9)	94(10)	−7(7)	48(8)	−18(7)
N(1)	4447(5)	2592(5)	904(5)	38(5)	42(5)	45(5)	3(4)	16(4)	−0(4)
N(2)	4465(5)	808(5)	1208(4)	29(4)	41(5)	34(4)	7(3)	12(3)	−1(4)
N(3)	331(6)	3150(6)	3189(5)	54(5)	60(6)	59(5)	−9(5)	30(4)	4(5)
N(4)	−1407(6)	3621(6)	2053(5)	56(6)	50(5)	61(6)	2(4)	31(5)	3(5)
N(5)	928(6)	3657(6)	1359(5)	51(5)	57(6)	48(5)	10(4)	14(4)	5(4)
N(6)	−792(6)	3086(6)	309(5)	47(5)	69(6)	43(5)	2(5)	9(4)	−9(5)
N(37)	2698(6)	1798(7)	1924(7)	49(6)	75(7)	116(8)	8(5)	44(6)	−2(6)
N(38)	6940(6)	1568(6)	1834(5)	42(5)	74(6)	48(5)	−10(5)	14(4)	−12(5)
N(39)	5452(8)	586(7)	3579(6)	101(9)	72(7)	85(8)	24(6)	44(7)	18(6)
O(1)	5190(6)	3073(5)	2547(4)	80(6)	64(5)	56(4)	−11(4)	25(4)	−19(4)
O(2)	−1336(5)	1466(5)	1575(5)	63(5)	58(5)	113(7)	−10(4)	54(5)	−16(5)
O(3)	982(6)	1509(6)	2071(6)	61(5)	85(7)	154(9)	16(5)	63(6)	7(6)
Na	−194(3)	2683(3)	1752(2)	51(2)	65(3)	56(2)	3(2)	28(2)	1(2)

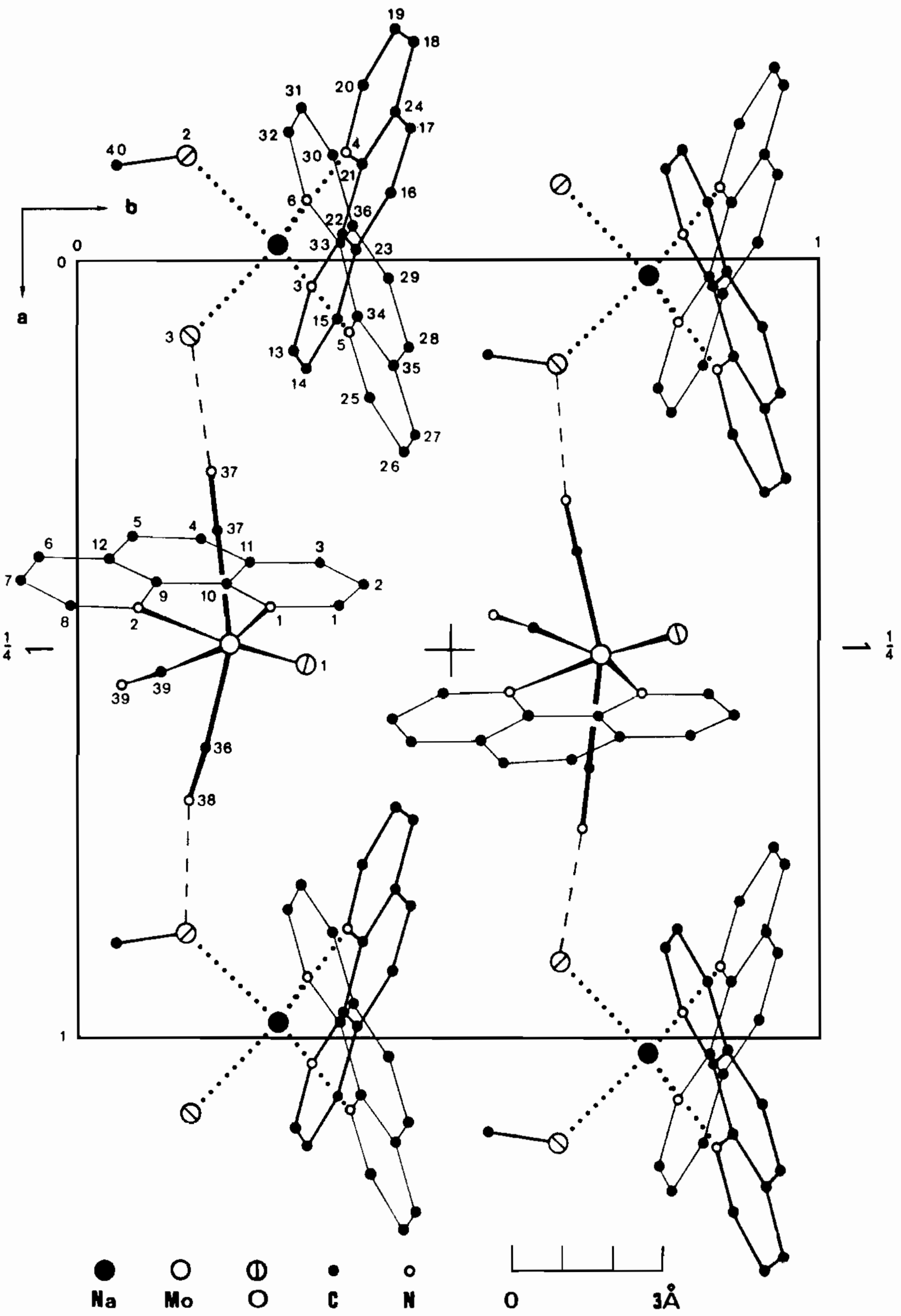

Fig. 1. Partial projection of the structure onto the (001) plane. Atoms numbered according to Table I. Dashed lines: hydrogen bonds. Dotted lines: ion-dipole interactions. Non-coded atoms refer to coordinates (1 + x, y, z), ($\bar{x}$, 1/2 + y, 1/2 – z) or (1 – x, 1/2 + y, 1/2 – z).

vation) agree well with those of Na[MoO(CN)$_3$-(phen)]·2phen. The oxygen atom in the complex anion exerts a marked structural *trans* influence so that the Mo–N(2) distance is 0.19 Å longer than the Mo–N(1) distance. Comparative bonding distances of 2.321(5) and 2.342(6) Å were reported [12] for the Mo(VI) dimer [Mo$_2$(phen)$_2$(NCS)$_2$O$_5$]·C$_3$H$_6$O. The three cyano groups in a *mer* configuration have two normal Mo–C$_{av}$ 2.15(1) Å bond distances and a significantly shorter Mo–C(39) 2.09(1) Å *trans* to the shorter Mo–N(1) bond. The fact that the N(1) atom has only σ-bonding capacity leads to extensive π-shortening of this Mo–C bond. This has to be correlated with the reasoning put forward for exactly the same phenomenon in Na[MoO(CN)$_3$(phen)]·2phen [5], as well as similar cases like those of [*cis*-Re(CH$_3$-

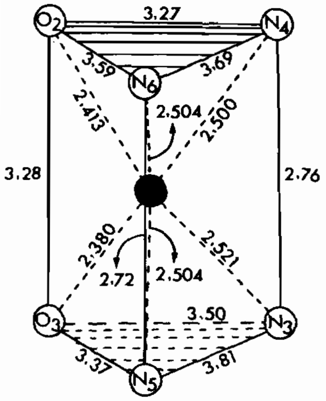

Fig. 2. Bond and edge lengths (Å) for the distorted trigonal prismatic environment of sodium ions. Atom numbering according to Table I.

$CN)_4(CO)_2]_2[ReCl_6]$ [13] and tetra-n-propylammonium bis(maleonitriledithiolato)-1,10-phenanthrolinecobaltate(II) [14].

The C(39)–N(39) bond is also somewhat longer than the normal expected value, which is in accord with the partial double bond character of the accompanying metal–carbon bond. The significant deviation from linearity for the Mo–C(38)–N(38) chain can be ascribed to packing considerations. The same effect was also observed in $Na[MoO(CN)_3(phen)]\cdot 2phen$ for one of the *cis*-orientated cyano groups, both of which were engaged in ion-dipole interactions with sodium ions. Since two *trans*-orientated cyano groups are engaged in the chain-like packing pattern of the present structure, it is not surprising that the same phenomenon occurs in a Mo–C≡N chain entirely different from the previous one.

This structure determination revealed that at a greater mol fraction of co-solvent, like methanol, it is possible to obtain a second solid crystalline phase from the phen–$MoO_2(CN)_4^{4-}$ reaction in solution. This finding also implies the non-existence

TABLE III. Selected van der Waals Distances (Å) with E.s.d.'s in Parentheses.

Bond type	Distance	Bond type	Distance
C(38)•••C(39)	2.98(2)	C(37)•••C(39)	2.91(1)
C(38)•••O(1)	2.98(1)	C(37)•••O(1)	2.96(1)
C(38)•••N(1)	2.98(1)	C(37)•••N(1)	3.03(2)
C(38)•••N(2)	2.87(1)	C(37)•••N(2)	2.87(1)
O(1)•••N(1)	2.86(1)	O(1)•••C(39)	2.98(1)
C(39)•••N(2)	3.12(1)		

TABLE II. Parameters for the $[MoO(CN)_3(phen)]^-$ Ion (E.s.d.s in Parentheses).

Bond and edge lengths (Å)					
Mo–O(1)	1.669(8)	O(1)–N(1)	2.86(1)	C(3)–C(11)	1.40(2)
Mo–N(1)	2.173(8)	O(1)–C(37)	2.96(1)	C(10)–C(11)	1.41(1)
Mo–N(2)	2.363(7)	O(1)–C(38)	2.98(1)	C(9)–C(10)	1.41(1)
Mo–C(37)	2.15(1)	O(1)–C(39)	2.98(1)	C(4)–C(11)	1.44(2)
Mo–C(38)	2.15(1)	N(1)–C(37)	3.03(2)	C(4)–C(5)	1.37(2)
Mo–C(39)	2.09(1)	N(1)–C(38)	2.98(1)	C(5)–C(12)	1.43(1)
C(37)–N(37)	1.15(2)	C(37)–C(39)	2.91(1)	C(9)–C(12)	1.42(1)
C(38)–N(38)	1.16(1)	C(38)–C(39)	2.98(2)	C(6)–C(12)	1.40(2)
C(39)–N(39)	1.20(2)	N(1)–C(1)	1.37(1)	C(6)–C(7)	1.39(2)
N(1)–N(2)	2.66(1)	N(1)–C(10)	1.39(1)	C(7)–C(8)	1.41(1)
N(2)–C(37)	2.87(1)	C(1)–C(2)	1.41(2)	N(2)–C(8)	1.34(1)
N(2)–C(38)	2.87(1)	C(2)–C(3)	1.38(2)	N(2)–C(9)	1.36(1)
N(2)–C(39)	3.12(1)				
Selected angles (°)					
N(1)–Mo–N(2)	71.6(3)	C(37)–Mo–C(38)	157.2(4)	C(1)–C(2)–C(3)	120.6(11)
N(2)–Mo–C(38)	78.8(3)	O(1)–Mo–N(2)	166.8(3)	C(6)–C(7)–C(8)	118.4(10)
N(2)–Mo–C(37)	78.7(3)	C(38)–N(1)–C(37)	89.1(3)	C(2)–C(3)–C(11)	118.7(11)
N(2)–Mo–C(39)	88.9(3)	N(1)–C(38)–C(39)	89.6(4)	C(7)–C(6)–C(12)	120.2(9)
O(1)–Mo–N(1)	95.2(3)	C(38)–C(39)–C(37)	91.4(4)	C(3)–C(11)–C(10)	118.9(10)
O(1)–Mo–C(37)	100.9(4)	N(1)–C(37)–C(39)	89.9(4)	C(6)–C(12)–C(9)	117.3(9)
O(1)–Mo–C(38)	101.8(4)	Mo–C(37)–N(37)	179.5(9)	N(1)–C(10)–C(11)	122.5(9)
O(1)–Mo–C(39)	104.3(4)	Mo–C(38)–N(38)	175.5(8)	N(2)–C(9)–C(12)	123.3(9)
N(1)–Mo–C(37)	89.0(4)	Mo–C(39)–N(39)	177.6(11)	C(9)–C(10)–C(11)	120.5(9)
C(37)–Mo–C(39)	86.8(4)	C(1)–N(1)–C(10)	117.5(9)	C(10)–C(9)–C(12)	119.9(8)
C(38)–Mo–C(39)	89.3(4)	C(8)–N(2)–C(9)	117.5(8)	C(4)–C(11)–C(10)	118.8(10)
N(1)–Mo–C(38)	87.3(3)	C(2)–C(1)–N(1)	121.7(10)	C(5)–C(12)–C(9)	119.2(9)
N(1)–Mo–C(39)	160.5(4)	C(7)–C(8)–N(2)	123.2(9)	C(5)–C(4)–C(11)	120.9(10)
				C(4)–C(5)–C(12)	120.6(10)

of a solid with composition $Na[MoO(CN)_3(phen)]\cdot 2phen\cdot xH_2O$ with water as the sole reaction solvent. It must be added that this reaction in water alone only yields crystals of $Na[MoO(CN)_3(phen)]\cdot 2phen$, but due to smaller size and abundance in twinning we originally added methanol and ethanol to improve solubilities of the product complex and phenanthroline. The cation–anion interactions in these structures take place either by direct interactions between cyano ligands and sodium ions, as in $Na[MoO(CN)_3(phen)]\cdot 2phen$, or via solvent molecules as indicated for the present structure. Given the chain-like array of Fig. 1, it is difficult to explain why a second water molecule cannot be visualized in place of a methanol molecule. The bond distances (*vide supra*) and angles (Na–O(3)–N(37) = 120.9(5)°, Na–O(2)–N(38′) = 126.7(4)°) for the oxygen atoms are also very similar. It thus seems as if the methanolic oxygen is a prerequisite for effective coulombic interaction between the cations and anions in this type of stacking pattern.

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