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(12) The plural is used since enantiomeric forms would exist.

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(14) The arguement that this is the threshold mechanism for proximal $\rightleftharpoons$ distal exchange in $W_2X_2(NEt_2)_4$ molecules (X = halide and alkyl) has been previously made in ref 13.

(15) The assignment of low field to proximal and high field distal R groups has previously been elaborated upon: M. H. Chisholm, F. A. Cotton, B. A. Frenz, W. W. Reichert, L. W. Shive, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 4469 (1976).

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Preparation of Tetraammonium Octakis(isothiocyanato)dimolybdenum(II) and Structural Characterization of Two Crystalline Hydrates

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By a ligand replacement reaction in aqueous solution the $[Mo_2(NCS)_8]^{4-}$ ion has been prepared and isolated in two compounds: $(NH_4)_4Mo_2(NCS)_8 \cdot 4H_2O$ (**1**) and $(NH_4)_4Mo_2(NCS)_8 \cdot 6H_2O$ (**2**). The structures of these deep blue-green substances have been determined by X-ray crystallography and the electronic absorption spectrum of the $[Mo_2(NCS)_8]^{4-}$ ion has been measured. Compound **1** crystallizes in space group *Pbca* with $a = 13.859$ (3) Å, $b = 13.012$ (4) Å, $c = 16.937$ (4) Å, $V = 3054$ Å^3, and $Z = 4$. Compound **2** crystallizes in space group $P\bar{1}$ with $a = 10.706$ (2) Å, $b = 11.708$ (3) Å, $c = 14.346$ (3) Å, $\alpha = 105.79$ (2)°, $\beta = 93.37$ (2)°, $\gamma = 105.71$ (2)°, $V = 1649$ (1) Å^3, and $Z = 2$. In **2** there are two crystallographically independent $[Mo_2(NCS)_8]^{4-}$ ions, each on an inversion center, and the $[Mo_2(NCS)_8]^{4-}$ in **1** also resides on an inversion center. All three crystallographically distinct anions have virtual D_{4h} symmetry with approximately linear MoNCS chains. The Mo–Mo distances are 2.162 (1) Å in **1** and 2.177 (1) and 2.174 (1) Å in **2**. These distances are slightly longer than Mo–Mo quadrupole bond distances previously observed in any compound except the allyl, $Mo_2(allyl)_4$. The small differences between the three Mo–Mo bond lengths appear to be due to differences in the intermolecular interactions. The NH_4^+ ions in each case are hydrogen bonded to water molecules. The visible spectrum contains a band at about 14 500 cm^{-1} which may be assigned to the $\delta \rightarrow \delta^*$ transition.

Introduction

The chemistry of quadruply bonded dinuclear complexes containing halide ions as ligands is quite extensive.[1] The ions $[Re_2Cl_8]^{2-}$, $[Mo_2Cl_8]^{4-}$, and $[Tc_2Cl_8]^{3-}$ were first recognized and characterized[2-4] more than a decade ago, and numerous derivatives are known in which halide ions are partly replaced to give complexes of the types $M_2L_4X_4$[5] or $M_2(LL)_2X_4$,[5,6] where L and LL represent mono- and bidentate phosphine, arsine, or alkyl sulfide type ligands. On the other hand, relatively little has yet been learned about the chemistry of comparable compounds with pseudohalogen ions as ligands. Even for the thiocyanate ion, which is perhaps the most obvious candidate to give comparable compounds, little has been done.

The $[Re_2(NCS)_8]^{2-}$ ion was reported[7] in 1967, and, more recently, the compound $Mo_2(dppm)_2(NCS)_4$ (where dppm = $Ph_2PCH_2PPh_2$) has been fully characterized.[8] We have also described the mixed (carboxylato)(thiocyanato)molybdenum species $Mo_2(O_2CR)_2(NCS)_4$, in which the carboxylate groups are the neutral, zwitterionic amino acids glycine and L-isoleucine.[9] In all of these compounds the NCS^- ligands are isothiocyanato groups; that is, they are bound to the metal atoms through the nitrogen atoms.

The objective of the present study was to prepare and characterize the simple $[Mo_2(NCS)_8]^{4-}$ ion, which has not previously been unambiguously shown to exist. Nimry and Walton,[10] while isolating a number of other NCS-containing dimolybdenum(II) complexes, were not successful in preparing any compound containing the $[Mo_2(NCS)_8]^{4-}$ ion. Hochberg and Abbott[11] described "highly air-sensitive...diamagnetic green needle-like crystals" to which they assigned the formula $(NH_4)_4Mo_2(NCS)_8(CH_3OCH_2CH_2OCH_3)_4$ on the basis of elemental analyses and spectroscopic data, but this substance has not been conclusively identified.[12] We report here that the $[Mo_2(NCS)_8]^{4-}$ ion can be isolated in the form of crystalline, hydrated ammonium salts, $(NH_4)_4[Mo_2(NCS)_8] \cdot xH_2O$, and we have carried out full structure determinations on those with $x = 4$ and 6.

Experimental Section

Preparation of $(NH_4)_4Mo_2(NCS)_8 \cdot 4H_2O$ (1) and $(NH_4)_4Mo_2(NCS)_8 \cdot 6H_2O$ (2). $K_4Mo_2Cl_8$ (0.02 g), prepared by a literature method,[4] was dissolved in 1 mL of 2 M NH_4NCS under argon. The deep turquoise solution was allowed to mix by diffusion through a glass frit with a saturated solution of NH_4NCS at 0 °C. Deep blue-green crystals were formed over a 24-h period. It was observed that a few crystals had an approximately cubic morphology while the majority were elongated plates with well-developed faces. The former were found to be orthorhombic and to contain compound **1** while the latter are triclinic and contain compound **2**. The structures of both have been determined.

X-ray Crystallography. Data were collected for both compounds on an Enraf-Nonius CAD-4F automatic diffractomator, using Mo Kα radiation ($\lambda_{\bar{\alpha}}$ 0.71073 Å) with a graphite crystal monochromator in the incident beam. The takeoff angle of the X-ray tube was 2.80° and the temperature during data collection was 26 ± 1 °C. The standard CAD-4 centering, indexing, and data collection programs were used.

Twenty-five reflections between 12° and 15° in θ were located by a random search procedure and subsequently centered. These reflections were used as the basis for the indexing. The cell constants and the orientation matrix that were obtained were refined by a least-squares fit.

The scan width for each reflection was determined as $0.8 + 0.347 \tan \theta$. Reflections were first measured with a scan rate of 20.12°/min. The rate for the final scan was calculated from the preliminary scan

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Table I. Crystallographic Data[a]

	$(NH_4)_4Mo_2(NCS)_8 \cdot 4H_2O$, **1**	$(NH_4)_4Mo_2(NCS)_8 \cdot 6H_2O$, **2**
space group	*Pbca*	$P\bar{1}$
a, Å	13.859 (3)	10.706 (2)
b, Å	13.012 (4)	11.708 (3)
c, Å	16.937 (4)	14.346 (3)
α, deg		105.79 (2)
β, deg		93.37 (2)
γ, deg		105.71 (2)
V, Å³	3054 (1)	1649 (1)
d(calcd), g/cm³	1.74	1.69
Z	4	2
crystal size, mm	0.15 × 0.15 × 0.15	0.15 × 0.1 × 0.1
μ, cm⁻¹	13.66	12.74
range of 2θ, deg	3–50	3–45
no. of unique data	2685	3259
data with $F_o^2 > 3\sigma(F_o^2)$	1741	2973
R_1	0.045	0.056
R_2	0.068	0.082
goodness of fit	1.48	1.74

[a] Numbers in parentheses following certain data are estimated standard deviations occurring in the least significant digit.

results so that the ratio $I/\sigma(I)$ would be at least 20 and the maximum scan time would not exceed 30 s. If in the preliminary scan $I/\sigma(I) \geq 20$, this measurement was used as the datum. Scan rates varied from 20.12 to 2.51°/min. All reflections were measured by using an ω–2θ motion. The width of the adjustable vertical aperture at the detector was given by (1.5 + tan θ) mm. The horizontal slit was 4 mm. Of the 96 steps in the scan, the first and last 16 steps were considered to be background. The formulas used to derive the intensity and its standard deviation were

$$I = [P - 2(B_1 + B_2)]S$$

$$\sigma(I) = [P + 4(B_1 + B_2)]^{1/2}S$$

where *P* is the gross peak intensity, B_1 and B_2 are the background intensities, and *S* is the scan rate.

During data collection, three intensity standards were measured after every hour of X-ray exposure. No decay was observed. In addition, three orientation standards were recentered after every 100 reflections to minimize the effects of crystal movement. If the standard deviation of the *h*, *k*, and *l* values for any orientation reflection exceeded 0.1, a new orientation matrix was calculated on the basis of the recentering of 22 reference reflections.

Crystallographic data and other pertinent information for the two compounds are given in Table I. For each crystal the data were corrected for Lorentz and polarization effects; because of the low μ values (Table I) no absorption correction was applied.

The heavy-atom positions in **1** were obtained from a three-dimensional Patterson function. The structure was refined[13] in space group *Pbca* to convergence by using anisotropic thermal parameters for all the nonhydrogen atoms. The heavy-atom positions in **2** were obtained by direct methods with the MULTAN program. This structure was refined in space group $P\bar{1}$ to convergence by using anisotropic thermal parameters for all the atoms except the ammonium nitrogen atoms and the water oxygen atoms.

The discrepancy indices

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

and

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$$

are listed in Table I.

The final difference maps showed no peaks of structural significance. Lists of the observed and calculated structure factors are available as supplementary material.

Results and Discussion

The addition of $K_4Mo_2Cl_8$ to an excess of 2 M NH_4NCS solution gives a clear solution that is intensely turquoise. From this solution, by slow diffusion of a saturated solution of NH_4NCS at 0 °C through a fritted glass disk, deep blue-green crystals of hydrated $(NH_4)_4[Mo_2(NCS)]_8$ are obtained. The color of these crystals is as much blue as it is green and can perhaps best be called turquoise. The substance prepared by Hochberg and Abbott had definitely more of a pure green color. However, we have also obtained compounds with other cations, such as K^+, in microcrystalline form, and these often had colors which were much more green than blue. It is likely that Hochberg and Abbott's compound also contains the $[Mo_2(NCS)_8]^{4-}$ ion.

Close examination of the crystalline product we obtained showed that there were at least two distinct types of crystal and the complete crystallographic characterization of each one revealed that they are different hydrates, namely, $(NH_4)_4[Mo_2(NCS)_8] \cdot 4H_2O$ (**1**) and $(NH_4)_4[Mo_2(NCS)_8] \cdot 6H_2O$ (**2**), each containing the same $[Mo_2(NCS)_8]^{4-}$ anion, although the exact dimensions of the anion vary a little. The positional and thermal parameters for **1** and **2** are listed in Tables II and III, respectively. The high thermal parameters for several water oxygen atoms in **2** suggest only partial occupancy.

In the tetrahydrate, **1**, there is only one crystallographically distinct $[Mo_2(NCS)_8]^{4-}$ ion, and it resides on a fourfold special position in space group *Pbca*, which has crystallographic inversion symmetry. In the hexahydrate, **2**, there are two independent $[Mo_2(NCS)_8]^{4-}$ ions, each of which occupies a crystallographic inversion center in space group $P\bar{1}$. In all then, there are three independent $[Mo_2(NCS)_8]^{4-}$ ions in the compounds studied. Tables IV and V report the bond lengths and angles for these and Figure 1 gives an ORTEP drawing of the anion. The numbering schemes used in all the tables are defined as follows. The numbers shown in Figure 1 are those

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $(NH_4)_4Mo_2(NCS)_8 \cdot 4H_2O$ (**1**)

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.55721 (4)	0.44363 (4)	0.00282 (3)	2.58 (2)	2.28 (2)	3.34 (2)	−0.17 (2)	0.17 (2)	−0.16 (2)
S(1)	0.8334 (1)	0.6667 (2)	0.0326 (2)	3.29 (7)	4.84 (9)	9.2 (1)	−1.27 (9)	−0.45 (9)	0.9 (1)
S(2)	0.4453 (2)	0.6840 (2)	−0.2730 (1)	7.2 (1)	8.1 (1)	4.97 (9)	1.9 (1)	1.33 (9)	2.58 (9)
S(3)	0.3901 (2)	0.1204 (1)	−0.0458 (1)	6.6 (1)	2.87 (7)	5.32 (9)	−1.61 (8)	−1.30 (8)	0.14 (7)
S(4)	0.3069 (2)	0.5289 (2)	0.2616 (1)	10.9 (2)	4.61 (9)	5.75 (9)	0.4 (1)	4.45 (9)	0.09 (8)
O(1)	0.2828 (4)	0.2729 (4)	0.2948 (3)	5.8 (3)	5.4 (3)	5.5 (2)	−0.3 (2)	−0.8 (2)	−0.4 (2)
O(2)	0.0775 (5)	0.6123 (5)	0.2924 (4)	9.4 (4)	6.1 (3)	9.2 (4)	−1.3 (3)	1.5 (3)	0.7 (3)
N(1)	0.6763 (4)	0.5377 (4)	0.0344 (3)	3.0 (2)	3.8 (2)	4.6 (2)	0.0 (2)	0.1 (2)	−1.1 (2)
N(2)	0.4519 (4)	0.6065 (4)	−0.1210 (3)	4.3 (2)	2.8 (2)	3.4 (2)	0.1 (2)	−0.2 (2)	0.2 (2)
N(3)	0.5174 (4)	0.6909 (4)	0.0267 (3)	3.2 (2)	2.5 (2)	3.9 (2)	−0.0 (2)	−0.1 (2)	0.1 (2)
N(4)	0.3883 (4)	0.5489 (4)	0.1127 (3)	3.2 (2)	3.7 (2)	4.3 (2)	−0.1 (2)	0.2 (2)	−0.8 (2)
N(5)	0.1762 (5)	0.7372 (6)	0.6296 (4)	6.9 (3)	8.4 (4)	3.6 (3)	−0.2 (4)	−0.2 (3)	0.1 (3)
N(6)	0.4605 (6)	0.4394 (6)	0.6372 (5)	12.2 (6)	9.8 (6)	5.3 (4)	−4.3 (5)	1.0 (4)	−0.9 (4)
C(1)	0.7419 (4)	0.5909 (5)	0.0343 (4)	2.1 (2)	3.2 (3)	4.7 (3)	−0.1 (2)	−0.0 (3)	−0.2 (3)
C(2)	0.4500 (4)	0.6391 (5)	−0.1837 (4)	3.3 (3)	2.8 (3)	4.4 (3)	0.4 (2)	0.5 (2)	−0.3 (2)
C(3)	0.4457 (4)	0.2294 (5)	−0.0348 (4)	3.2 (3)	2.7 (3)	3.2 (2)	0.5 (2)	−0.6 (2)	−0.3 (2)
C(4)	0.3523 (5)	0.5403 (5)	0.1741 (4)	4.3 (3)	2.5 (3)	4.4 (3)	0.4 (3)	0.6 (3)	−0.1 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for $(NH_4)_4Mo_2(NCS)_8 \cdot 6H_2O$ (**2**)

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.96422 (8)	0.51332 (7)	0.57047 (6)	3.00 (3)	1.99 (3)	3.27 (3)	0.20 (3)	0.12 (3)	0.63 (2)
Mo(2)	0.05857 (8)	0.97845 (7)	0.94202 (6)	3.07 (3)	2.27 (3)	3.62 (4)	0.24 (3)	0.15 (3)	0.61 (3)
S(1)	0.3885 (3)	0.8710 (3)	0.4837 (3)	4.5 (1)	4.2 (1)	11.1 (2)	−0.9 (1)	−0.4 (2)	3.6 (1)
S(2)	0.3847 (3)	0.3090 (3)	0.4901 (3)	5.5 (1)	7.3 (1)	9.0 (2)	3.8 (1)	1.7 (1)	3.1 (1)
S(3)	1.2357 (3)	0.9288 (3)	0.7630 (2)	5.0 (1)	3.3 (1)	4.9 (1)	−0.9 (1)	0.8 (1)	−0.5 (1)
S(4)	1.2173 (4)	0.3488 (3)	0.7641 (3)	9.0 (2)	10.0 (2)	6.4 (1)	5.4 (1)	1.0 (1)	4.4 (1)
S(11)	−0.1327 (4)	0.5311 (3)	0.7872 (2)	7.9 (2)	2.8 (1)	5.4 (1)	0.1 (1)	2.0 (1)	0.2 (1)
S(12)	0.4026 (3)	1.3698 (3)	1.0035 (3)	4.7 (2)	3.8 (1)	12.1 (2)	−0.6 (1)	1.1 (2)	2.6 (1)
S(13)	−0.1611 (4)	1.0854 (4)	0.6857 (3)	9.0 (2)	12.3 (2)	6.7 (1)	3.2 (2)	0.1 (2)	5.7 (1)
S(14)	0.4267 (4)	0.8787 (5)	1.0827 (4)	7.9 (2)	14.1 (3)	11.7 (3)	6.3 (1)	−0.9 (2)	3.6 (2)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Ow(1)	−0.018 (1)	0.3225 (9)	0.9256 (8)	8.6 (3)	Ow(4)	0.320 (1)	0.2217 (11)	0.2104 (9)	10.6 (3)
Ow(2)	0.001 (1)	0.1406 (9)	0.4864 (7)	8.1 (3)	Ow(5)	0.480 (2)	0.7423 (17)	0.2608 (14)	21.6 (9)
Ow(3)	0.374 (1)	0.6304 (10)	0.6573 (8)	9.0 (3)	Ow(6)	0.261 (2)	0.6770 (20)	0.8568 (16)	21.0 (8)

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
N(1)	0.1827 (8)	0.6545 (7)	0.4561 (6)	3.3 (3)	2.7 (3)	5.3 (4)	−0.3 (3)	0.5 (3)	1.4 (3)
N(2)	0.1845 (8)	0.4070 (7)	0.4521 (6)	3.5 (3)	3.2 (3)	4.8 (4)	0.9 (3)	0.7 (3)	0.9 (3)
N(3)	1.0868 (8)	0.6943 (7)	0.6487 (6)	3.7 (4)	3.0 (3)	3.7 (3)	−0.1 (3)	0.3 (3)	0.8 (3)
N(4)	1.0842 (8)	0.4388 (7)	0.6416 (6)	4.3 (4)	3.8 (3)	4.0 (3)	1.4 (3)	0.5 (3)	1.7 (3)
N(11)	−0.0328 (8)	0.7879 (7)	0.8785 (6)	4.0 (4)	2.5 (3)	4.8 (4)	0.2 (3)	0.5 (3)	0.4 (3)
N(12)	0.1987 (8)	1.1537 (8)	0.9670 (6)	4.1 (4)	3.6 (3)	4.3 (4)	0.7 (3)	1.0 (3)	0.8 (3)
N(13)	−0.0445 (8)	1.0148 (8)	0.8299 (6)	3.9 (4)	4.4 (4)	3.7 (3)	0.6 (3)	0.0 (3)	1.1 (3)
N(14)	0.2039 (8)	0.9296 (7)	1.0136 (6)	4.0 (4)	4.7 (4)	4.4 (4)	1.5 (3)	0.1 (3)	1.6 (3)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
N(21)	0.209 (1)	0.079 (1)	0.5870 (9)	8.3 (3)	N(23)	0.453 (2)	0.497 (1)	0.2762 (12)	11.2 (5)
N(22)	0.461 (1)	0.103 (1)	0.3009 (9)	8.2 (3)	N(24)	0.208 (1)	0.557 (1)	−0.0009 (10)	9.4 (4)

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0.2657 (9)	0.7416 (9)	0.4666 (7)	3.5 (4)	4.5 (4)	4.0 (4)	1.4 (3)	0.3 (4)	1.6 (3)
C(2)	0.2690 (10)	0.3682 (9)	0.4669 (7)	3.6 (4)	3.1 (4)	4.0 (4)	0.2 (4)	1.0 (4)	0.6 (3)
C(3)	1.1488 (9)	0.7915 (9)	0.6944 (7)	3.1 (4)	3.1 (4)	3.8 (4)	0.2 (3)	−0.0 (4)	0.9 (3)
C(4)	1.1379 (11)	0.4018 (9)	0.6922 (7)	6.0 (5)	3.6 (4)	4.0 (4)	1.1 (4)	1.4 (4)	1.6 (3)
C(11)	−0.0769 (10)	0.6816 (9)	0.8394 (7)	4.2 (4)	3.7 (4)	3.5 (4)	0.8 (4)	1.4 (4)	1.2 (3)
C(12)	0.2848 (10)	1.2454 (9)	0.9813 (8)	4.3 (5)	2.7 (4)	5.1 (5)	0.6 (4)	0.7 (4)	0.2 (4)
C(13)	−0.0910 (11)	1.0411 (11)	0.7680 (8)	4.2 (5)	6.0 (5)	5.3 (5)	0.9 (4)	1.2 (4)	2.4 (4)
C(14)	0.2957 (12)	0.9092 (12)	1.0410 (9)	5.9 (6)	6.1 (6)	5.4 (6)	1.9 (5)	−0.0 (5)	0.9 (5)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

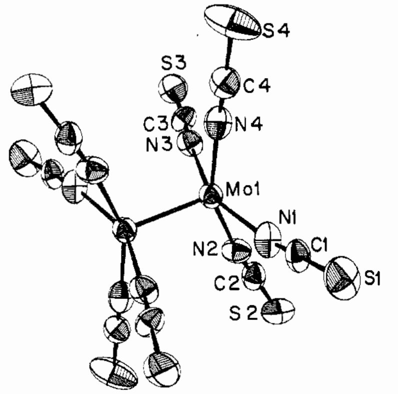

Figure 1. An ORTEP drawing of the $[Mo_2(NCS)_8]^{4-}$ unit. The numbering scheme applies to all three crystallographically unique ones, as explained in the text. Each atom is represented by its ellipsoid of vibration scaled to enclose 50% of the electronic density.

Table IV. Bond Distances and Bond Angles for $(NH_4)_4Mo_2(NCS)_8 \cdot 4H_2O$ (**1**)

	Distance (Å)		
Mo(1)–Mo(1)′	2.162 (1)	Mo(1)–N(3)	2.093 (6)
N(1)	2.123 (5)	N(4)	2.099 (6)
N(2)	2.109 (5)		
S(1)–C(1)	1.607 (5)	N(1)–C(1)	1.143 (6)
S(2)–C(2)	1.624 (6)	N(2)–C(2)	1.143 (7)
S(3)–C(3)	1.625 (6)	N(3)–C(3)	1.165 (8)
S(4)–C(4)	1.617 (7)	N(4)–C(4)	1.159 (9)
	Angle (deg)		
Mo(1)′–Mo(1)–N(1)	100.9 (1)	Mo(1)–N(1)–C(1)	165.4 (4)
N(2)	102.0 (1)	N(2)–C(2)	174.0 (4)
N(3)	101.2 (1)	N(3)–C(3)	171.7 (5)
N(4)	101.0 (2)	N(4)–C(4)	174.6 (6)
N(1)–Mo(1)–N(2)	89.2 (2)		
N(3)	157.8 (2)	S(1)–C(1)–N(1)	178.8 (4)
N(4)	85.9 (2)	S(2)–C(2)–N(2)	178.8 (6)
N(2)–Mo(1)–N(3)	86.5 (2)	S(3)–C(3)–N(3)	177.7 (6)
N(4)	157.0 (2)	S(4)–C(4)–N(4)	177.3 (7)
N(3)–Mo(1)–N(4)	89.6 (2)		

for the anion in compound **1** and for molecule I in compound **2**. The ligand atoms of molecule II in compound **2** have numbers equal to those shown plus 10.

As in all previous cases where the thiocyanate ion is a ligand toward a quadruply bonded dimetal cation, the thiocyanate ions in the $[Mo_2(NCS)_8]^{4-}$ ion are N-bonded (i.e., isothiocyanato) ligands. There is no significant variation in any of the distances or angles in the Mo–N–C–S moiety over the 12 equivalent ones that are found in these two structures. The mean values are listed in Table VI. Clearly, the N–C–S ligands are essentially linear, while there is a small but persistent deviation from linearity in the Mo–N–C chains. The slightly obtuse Mo–Mo–N angle, 100.9°, is quite characteristic of $[M_2X_8]^{4-}$ ions.

The $[Mo_2(NCS)_8]^{4-}$ ions each reside on an inversion center and since the N–Mo–N angles are all within the narrow range of 85.9–89.7° the ions have approximately D_{4h} symmetry. The major variation from one independent $[Mo_2(NCS)_8]^{4-}$ ion to another is in the Mo–Mo distances. In **1** this distance is 2.162 (1) Å, while in **2** the values are 2.174 (1) and 2.177 (1) Å. It appears that this variation (which is insignificant between

Table V. Bond Distances and Bond Angles for $(NH_4)_4Mo_2(NCS)_8 \cdot 6H_2O$ (**2**)

Molecule I			
Distance (Å)			
Mo(1)-Mo(1)′	2.177 (1)	Mo(1)-N(3)	2.121 (7)
N(1)	2.081 (7)	N(4)	2.095 (7)
N(2)	2.101 (7)		
S(1)-C(1)	1.664 (9)	N(1)-C(1)	1.12 (1)
S(2)-C(2)	1.634 (9)	N(2)-C(2)	1.15 (1)
S(3)-C(3)	1.624 (9)	N(3)-C(3)	1.14 (1)
S(4)-C(4)	1.645 (8)	N(4)-C(4)	1.14 (1)
Angle (deg)			
Mo(1)′-Mo(1)-N(1)	100.5 (2)	Mo(1)-N(1)-C(1)	176.0 (7)
N(2)	101.0 (2)	N(2)-C(2)	177.1 (7)
N(3)	101.1 (2)	N(3)-C(3)	176.6 (7)
N(4)	100.1 (2)	N(4)-C(4)	169.0 (7)
N(1)-Mo(1)-N(2)	87.3 (3)		
N(3)	158.4 (3)	S(1)-C(1)-N(1)	179.3 (8)
N(4)	87.4 (3)	S(2)-C(2)-N(2)	177.5 (8)
N(2)-Mo(1)-N(3)	88.2 (3)	S(3)-C(3)-N(3)	178.0 (9)
N(4)	158.8 (3)	S(4)-C(4)-N(4)	179.1 (8)
N(3)-Mo(1)-N(4)	89.1 (3)		
Molecule II			
Distance (Å)			
Mo(2)-Mo(2)′	2.174 (1)	Mo(2)-N(13)	2.098 (7)
N(11)	2.091 (7)	N(14)	2.102 (7)
N(12)	2.112 (7)		
S(11)-C(11)	1.638 (9)	N(11)-C(11)	1.16 (1)
S(12)-C(12)	1.588 (8)	N(12)-C(12)	1.17 (1)
S(13)-C(13)	1.632 (9)	N(13)-C(13)	1.15 (1)
S(14)-C(14)	1.657 (9)	N(14)-C(14)	1.14 (1)
Angle (deg)			
Mo(2)′-Mo(2)-N(11)	101.1 (2)	Mo(2)-N(11)-C(11)	175.4 (7)
N(12)	100.8 (2)	N(12)-C(12)	173.9 (7)
N(13)	99.7 (2)	N(13)-C(13)	174.2 (8)
N(14)	101.3 (2)	N(14)-C(14)	168.2 (7)
N(11)-Mo(2)-N(12)	158.0 (3)		
N(13)	89.7 (3)	S(11)-C(11)-N(11)	177.2 (9)
N(14)	87.0 (3)	S(12)-C(12)-N(12)	178.5 (8)
N(12)-Mo(2)-N(13)	88.7 (3)	S(13)-C(13)-N(13)	175.8 (9)
N(14)	86.7 (3)	S(14)-C(13)-N(13)	178.6 (9)
N(13)-Mo(2)-N(14)	159.0 (3)		

Table VI. Mean Bond Lengths and Angles in the $[Mo_2(NCS)_8]^{4-}$ Ion[a]

atoms	dist, Å	atoms	angle, deg
Mo-N	2.102 ± 0.009	Mo-Mo′-N	100.9 ± 0.4
S-C	1.629 ± 0.015	Mo-N-C	173 ± 3
C-N	1.148 ± 0.011	N-C-S	178.0 ± 0.8

[a] Error intervals are mean deviations from the unweighted arithmetic mean values.

the last two) can be attributed to intermolecular interactions. In each structure the $[Mo_2(NCS)_8]^{4-}$ ions are packed in such a way that each molybdenum atom is approached in the axial direction by a sulfur atom from a neighbor, but the closeness of approach varies. In **1** we have a Mo(1)···S(1)′ distance of 3.94 Å, whereas in **2** we have Mo(1)···S(11) = 3.31 Å and Mo(2)···S(3) = 3.30 Å. The two closer and essentially equal Mo···S distances are found with the two longer and essentially equal Mo–Mo distances while the very long Mo···S distance is found with the shorter Mo–Mo distance. This is consistent with the type of inverse relation generally observed for axial coordination in quadruply bonded M_2 species.[14]

Even the Mo–Mo distance in **1** where there is the least axial interaction has a length, 2.162 (1) Å, that is longer than the Mo–Mo distances seen in any other $[Mo_2X_8]^{4-}$ ion. For $[Mo_2Cl_8]^{4-}$, distances of 2.134 (1)–2.150 (5) Å have been found[15] and for $[Mo_2Br_8]^{4-}$ the reported[16] distance is 2.135 (2) Å. In fact, the $[Mo_2(NCS)_8]^{4-}$ ion has the longest Mo–Mo quadruple bond distance known, except for that, 2.183 (2) Å, found in the allyl molecule, $Mo_2(C_3H_5)_4$, which is a distinctly different structure,[17] and the recently reported distance of 2.167 (3) Å in $Mo_2(dmmp)_2(NCS)_4$.[8] If we take the distances of 2.174 (1) and 2.177 (1) Å in **2**, then even the latter is surpassed by $[Mo_2(NCS)_8]^{4-}$.

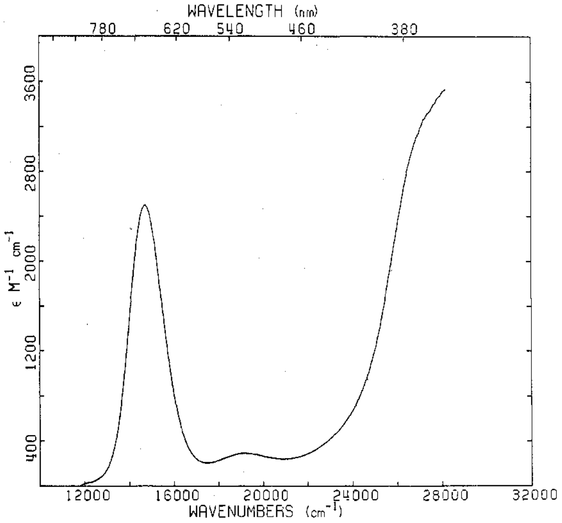

Figure 2. Absorption spectrum of $[Mo_2(NCS)_8]^{4-}$ in 1 M KNCS solution, recorded on a Cary 17-D spectrometer at 22 °C.

It is not certain why the isothiocyanato ligand causes the Mo–Mo quadrupole bond to be longer in $[Mo_2(NCS)_8]^{4-}$ than it is in $[Mo_2Cl_8]^{4-}$ and $[Mo_2Br_8]^{4-}$, but it is noteworthy that the same effect is observed in the $Mo_2(dppm)_2X_4$ molecules where the Mo–Mo distance is 2.138 (1) Å for X = Cl and 2.167 (3) Å for X = NCS. It would be interesting to know if it has a similar effect on the Re–Re quadruple bond.

The visible absorption spectrum of an aqueous solution of the $[Mo_2(NCS)_8]^{4-}$ ion is shown in Figure 2. The absorption band at 14 500 cm^{-1} presumably corresponds to the one at about 19 000 cm^{-1} in the $[Mo_2Cl_8]^{4-}$ spectrum and the latter has been assigned[18] to the $\delta \rightarrow \delta^*$ transition. The shift of over 4000 cm^{-1} indicates a weaker δ bond and this is consistent with the longer Mo–Mo distance in the isothiocyanate, although the situation may be more complicated than that. It may be noted that there is a similar bathochromic shift in going from $[Re_2Cl_8]^{2-}$ (14 500 cm^{-1}) to $[Re_2(NCS)_8]^{2-}$ where the lowest energy band observed is at 9000–10 000 cm^{-1}.

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Supplementary Material Available: Tables of observed and calculated structure factors for both compounds (21 pages). Ordering information is given on any current masthead page.

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The Tetrakis(hydrogen phosphato)dimolybdenum Ion $[Mo_2(HPO_4)_4]^{2-}$. Compounds with a Metal–Metal Triple Bond Which Are Easily Prepared and Permanently Stable in Air

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The octachlorodimolybdate(II) ion, $[Mo_2Cl_8]^{4-}$, reacts with 2 M orthophosphoric acid in air to form the purple $[Mo_2(HPO_4)_4]^{2-}$ ion which can easily be isolated in combination with various cations, for example, as $Cs_2[Mo_2(HPO_4)_4(H_2O)_2]$, **1**, and $(C_5NH_6)_3[Mo_2(HPO_4)_4]Cl$, **2**, both of which have been fully characterized structurally. They are stable indefinitely in ordinary air at 25 °C. The $[Mo_2(HPO_4)_4]_2^{2-}$ ion has a paddlewheel structure very similar to that of the $[Mo_2(SO_4)_4]^{4-,3-}$ ions; the manner in which the rings are bent and the placement of the hydrogen atoms are such as to make the idealized symmetry C_{4h}. The Mo–Mo triple bond lengths are 2.223 (2) and 2.232 (1) Å in **1** and **2**, respectively. In each case there are axial ligands, but these are loosely bonded with Mo–OH_2 distances of 2.46 (1) and 2.53 (1) Å in **1** and Mo–Cl distances of 2.910 (1) Å in **2**. In **1** there is no crystallographically imposed symmetry, but the conformation is only 1.35° from being precisely eclipsed, while in **2** there is $2/m$ crystallographic symmetry and the conformation is perfectly eclipsed. Compound **1** crystallizes in space group $P2_1/c$ with $a = 8.751$ (3) Å, $b = 11.217$ (3) Å, $c = 17.938$ Å, $\beta = 90.92$ (2)°, $V = 1761$ (1) Å^3, and $Z = 4$. Compound **2** crystallizes in space group $Pbam$ with $a = 18.329$ (3) Å, $b = 9.157$ (2) Å, $c = 8.053$ (1) Å, $V = 1351$ (1) Å^3, and $Z = 2$.

Introduction

The results we report here are of unusual interest in the field of multiple metal-to-metal bonds in two respects. One concerns the redox behavior of metal–metal quadruple bonds and the other has to do with the stability and other properties of triple bonds between metal atoms.

Previous attempts to generate triple bonds from quadruple bonds by oxidation to remove both electrons from the δ-bonding orbital have been unsuccessful. The earliest such attempt was with the $[Re_2X_8]^{2-}$ ions using X_2 (X = Cl, Br) as the oxidizing agent.[1] The desired two-electron oxidation occurred, but this was followed (or accompanied) by a structural rearrangement to give the bioctahedral ions, $[Re_2X_9]^-$. The $[Mo_2(SO_4)_4]^{4-}$ ion can be oxidized without gross structural change but only by one electron, to give the $[Mo_2(SO_4)_4]^{3-}$ ion,[2] which is now well characterized as having a bond order of 3.5. McCarley and co-workers[3] have shown that iodine removes only one electron from $Mo_2(O_2CCMe_3)_4$ and $MoW(O_2CCMe_3)_4$ to give the +1 ions with bond orders of 3.5. Most recently, the action of Br_2 and I_2 on $Mo_2(S_2COEt)_4$ was shown to give products with the formula $Mo_2(S_2COEt)_4X_2$ in which, again, there has been extensive rearrangement and reduction of the Mo–Mo bond order all the way to unity.[4]

We can now report the first successful attempt to carry out the two-electron oxidation of a quadruple bond to yield a triple bond, the reaction in question being, formally

$$[Mo_2Cl_8]^{4-} + 4HPO_4^{2-} + 2H^+ + {}^1/_2O_2 \rightarrow [Mo_2(HPO_4)_4]^{2-} + 8Cl^- + H_2O$$

The product of this reaction, $[Mo_2(HPO_4)_4]^{2-}$, is intrinsically interesting in comparison with previously known molecules and ions containing M≡M bonds.[5] From the structural point of view it is unique in being a discrete species with a $\sigma^2\pi^4$ type triple bond[6] in an environment of regular fourfold symmetry with an eclipsed configuration. From the chemical point of view it is also unique in its stability toward water and air at 25 °C.

Table I. Crystallographic Data

	$Cs_2[Mo_2(HPO_4)_4\cdot 2H_2O]$, 1	$(pyH)_3Mo_2(HPO_4)Cl$, 2
space group	$P2_1/c$	$Pbam$
a, Å	8.751 (3)	18.329 (3)
b, Å	11.217 (3)	9.157 (2)
c, Å	17.938 (4)	8.053 (1)
β, deg	90.92 (2)	
V, Å^3	1761 (1)	1351 (1)
d, g/cm^3	3.31	2.09
Z	4	2
μ, cm^{-1}	59.88	13.29
range of 2θ, deg	3 → 50	3 → 45
no. of unique data	2171	1081
data with $F_o^2 > 3\sigma(F_o^2)$	1900	1046
R_1	0.050	0.042
R_2	0.078	0.072
goodness of fit	1.65	1.84

Experimental Section

Preparations. $\mathbf{Cs_2[Mo_2(HPO_4)_4\cdot 2H_2O]}$**, 1.** $K_4Mo_2Cl_8\cdot 2H_2O$ (0.05 g), prepared by a literature method,[7] was dissolved in 20 mL of an aqueous solution (2 M) of H_3PO_4. CsCl (0.02 g) was added and the solution was left to stand in an open beaker. After 2 days, purple crystals were obtained.

$\mathbf{(C_5NH_6)_3[Mo_2(HPO_4)_4\cdot Cl]}$**, 2.** This compound was prepared in a way analogous to the Cs salt by using pyridinium chloride (0.03 g). The purple crystals were obtained after 24 h.

X-ray Crystallography. Collection of Data. Data were collected for both compounds on a Syntex P$\bar{1}$ automated four-circle diffractometer using Mo (λ 0.71073 Å) radiation with a graphite-crystal monochromator in the incident beam. Rotation photographs and ω scans of several strong reflections indicated in each case that the crystals were of satisfactory quality. The unit cell dimensions were obtained by a least-squares fit of 15 strong reflections in the range 25° < 2θ < 35°. Data were collected at 22 ± 3 °C by use of the θ–2θ scan technique with a variable scan rate from 4.0 to 24°/min. General procedures for data collection have been reported elsewhere.[8a]

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