(25) R. D. Archer, L. J. Suydan, and D. D. Dollberg, *J. Am. Chem. Soc.*, **93**, 6837 (1971).
(26) This suggestion was made by R. J. P. Williams at the Sixth International Conference on Coordination Chemistry, Detroit, Mich., 1961, in the discussion of D. Margerum's paper on the iron(II) diimine reactions and has been resurrected in detail by R. D. Gillard, *Coord. Chem. Rev.*, **16**, 67 (1975).
(27) D. D. Dollberg and R. D. Archer, *Inorg. Chem.*, **14**, 1888 (1975).

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Crystal and Molecular Structure of *trans*-Oxochlorotetrakis(methyl isocyanide)molybdenum(IV) Triiodide

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The synthesis and characterization of cationic molybdenum(IV) oxohalo isocyanide complexes have been described.[1] Here we report the x-ray crystal structure of $[MoOCl(CNCH_3)_4]I_3$. The relationship between this complex and other isocyanide and cyanide complexes of molybdenum is discussed elsewhere.[2]

Experimental Section

Collection and Reduction of X-Ray Data. Maroon-red needles of $[MoOCl(CNCH_3)_4](I_3)$[1] were obtained by slow evaporation of solvent from a nitromethane–methanol solution. Approximate unit cell parameters and the space group were determined on a precession camera using nickel-filtered Cu Kα radiation (λ 1.5418 Å). From the Laue symmetry C_{2h} $(2/m)$ and observed extinctions hkl, $h + k \neq 2n$, the space group was determined to be $C2$ [C_2^3; No. 5], Cm [C_s^3; No. 8], or $C2/m$ [C_{2h}^3; No. 12].

Using a Picker FACS-I-DOS diffractometer, data were collected on an irregular hexagonal prism with faces (210) and ($\bar{2}\bar{1}0$) 0.45 mm apart, ($2\bar{1}0$) and ($\bar{2}10$) 0.45 mm apart, (100) and ($\bar{1}00$), 0.06 mm apart, and (201) and ($\bar{2}0\bar{1}$) 0.050 mm apart. The crystal mounting was nearly along [$\bar{1}40$], which approximates the needle axis. The details of data collection are given in Table I. The apparatus, experimental technique, and data reduction were as described previously.[3] The orientation matrix used for data collection and the lattice parameters were computed from least-squares refinement of the setting angles of 12 carefully centered reflections.

Determination and Refinement of the Structure. An origin-removed, sharpened Patterson map revealed the positions of the iodine and molybdenum atoms, one carbon atom, and one nitrogen atom.[4] A structure factor calculation and difference Fourier map in space group Cm showed the oxygen atom of the Mo=O moiety and the chlorine atom to be disordered in such a manner as to be related by a twofold axis. Subsequent refinement was carried out in space group $C2/m$, with the Mo, O, and Cl atoms equally disordered in sites $x, 0, z$, and $\bar{x}, 0, \bar{z}$ and assigned half-weights. The higher symmetry of this space group requires the terminal iodine atoms of the triiodide anion to be related by a C_2 operation and is consistent with the Patterson map solution and with refinement in Cm.

Because of the small value of the lattice parameter β in $C2/m$, the hkl indices and atomic coordinates were transformed to the nonstandard space group $I2/m$ (Table I), in which all subsequent computations were made. Least-squares refinement, minimizing the function $\sum w(|F_o| - |F_c|)^2$ with weights $w = 4F_o^2/\sigma^2(F_o^2)$, converged at final values of 0.042 and 0.078 for $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$, respectively. No final parameter shift was greater than 0.071 times its estimated standard deviation. All atoms were assigned anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. A total of 56 parameters were varied to fit 855 data for which $F_o^2 > 2\sigma(F_o^2)$. In all calculations of F_c, the atomic scattering factors and anomalous dispersion corrections for iodine, molybdenum, and chlorine were taken from ref 5.

The error on an observation of unit weight, $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, was estimated to be 2.459; since $\sum w\Delta^2$ was fairly independent of $|F_o|$ and of $(\sin \theta)/\lambda$, no compensating weighting scheme was applied. An attempt to locate and refine the hydrogen atoms was unsuccessful. A final difference Fourier map showed residual electron density of ~1.51 e/Å^3 near the triiodide ion and less than 0.77 e/Å^3 elsewhere.

Table I. Experimental Data for the X-Ray Diffraction Study of $[MoOCl(CNCH_3)_4](I_3)$

(A) Crystal Parameters at 23 ± 1 °C[a]

Space group [C_{2h}^3; No. 12]	$C2/m$	$I2/m$
a, Å	17.024 (10)	6.068 (4)
b, Å	10.670 (9)	10.670 (9)
c, Å	6.068 (4)	15.087 (10)
cos β	0.4791 (3)	−0.1385 (3)
β, deg	61.37 (3)	97.96 (3)
V, Å^3	967.4	967.4
Z	2	
Mol wt	692.3	
ρ(calcd), g cm^{-3}	2.376	
ρ(obsd), g cm^{-3} (by neutral buoyancy in CH_3I–CH_2I_2)	2.37 (1)	

(B) Measurement of Intensity Data

Radiation: graphite-monochromatrized Mo Kα (λ 0.71069 Å)
Attenuators: used for counts >10,000/s
Takeoff angle: 2.15°
Detector aperture: 6.25 mm × 6.25 mm
Crystal–dectector distance: 33 cm
Scan mode: coupled θ(crystal)–2θ(counter)
Scan speed: 1°/min
Range: $2.7 < 2\theta < 50°$
Scan length: from $2\theta(K\alpha_1) - 1°$ to $2\theta(K\alpha_2) + 1°$
Background measurement: stationary crystal, stationary counter; 20 s at beginning and end of each 2θ scan
Std reflections: three remeasured every 97 reflections; an isotropic linear decay correction was applied to compensate for a 6% intensity loss owing to decomposition over the 140-h data collection period
Reflections collected: 2194 including two or more equivalent forms averaged[b] to give 989 unique data with $R_{F_o^2}(\text{av}) = 0.057$

(C) Reduction of Intensity Data

Conversion to F_o^2 and $\sigma(F_o^2)$: as in ref 3 with $\epsilon = 0.05$
Absorption coeff: $\mu = 52.2$ cm^{-1}; minimum and maximum transmission coefficients were 0.71 and 0.80, respectively[c]

[a] Data were collected and reduced with crystal parameters corresponding to $C2/m$. Final refinement and all reported results refer to the nonstandard setting $I2/m$. [b] Using AVERAGE by J. T. Gill. [c] Absorption corrections were carried out using a local version of ORABS, the Wehe–Busing–Levy program, adapted to the Picker FACS geometry.

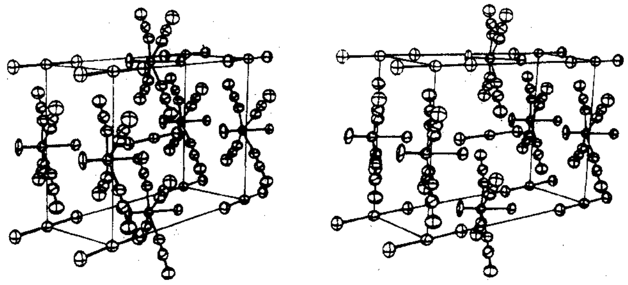

Figure 1. Stereoscopic view of the unit cell packing. The cation is shown as ordered for the purpose of this illustration (see text).

Final parameters are given in Table II and the molecular geometry is summarized in Table III. A listing of observed and calculated structure factor amplitudes and a table of root-mean-square amplitudes of vibration are available.[6] The unit cell packing is shown in Figure 1, and the molecular geometry and atom labeling scheme, in Figure 2.

Discussion

The coordination geometry of the $[MoOCl(CNCH_3)_4]^+$ cation has the chloride and oxygen atoms in trans positions, as suggested previously.[1] The site symmetry is close to C_{4v}, with the molybdenum atom displaced toward the oxygen by 0.33 Å from the plane defined by the four coordinated methyl

Table II. Final Positional and Thermal Parameters of the Atoms[a,b]

Atom	x	y	z	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I_1	0.0	0.0	0.0	0.0286 (3)	0.0073 (1)	0.0051 (1)	0.0	−0.0001 (1)	0.0
I_2	0.9737 (1)	0.0	−0.1943 (1)	0.0406 (4)	0.0124 (1)	0.0050 (1)	0.0	0.0010 (1)	0.0
Mo	0.4677 (4)	0.0	0.5164 (2)	0.0197 (9)	0.0069 (2)	0.0047 (2)	0.0	0.0012 (2)	0.0
Cl	0.6599 (13)	0.0	0.3823 (7)	0.0221 (17)	0.0095 (8)	0.0059 (4)	0.0	0.0022 (7)	0.0
C_1	0.2717 (14)	0.1379 (7)	0.4395 (6)	0.0312 (23)	0.0076 (8)	0.0057 (4)	0.0017 (12)	−0.0015 (8)	0.0008 (5)
N_1	0.1412 (11)	0.2075 (7)	0.4045 (5)	0.0297 (20)	0.0083 (7)	0.0078 (4)	−0.0014 (11)	0.0029 (8)	−0.0004 (5)
C_{11}	−0.0292 (14)	0.2866 (10)	0.3622 (6)	0.0374 (29)	0.0121 (10)	0.0065 (5)	0.0058 (15)	−0.0041 (10)	0.0019 (6)
O	0.3162 (73)	0.0	0.5980 (30)	0.1215 (241)	0.0175 (47)	0.0164 (35)	0.0	0.0397 (79)	0.0

[a] Atoms are labeled as indicated in Figure 2. [b] Standard deviations, in parentheses, occur in the last significant figure for each parameter. [c] The form of the anisotropic thermal ellipsoid is as defined in the text.

Table III. Intramolecular Bond Distances (Å) and Angles (deg)[a]

Distances			
I_1-I_2	2.914 (2)	Mo-C_1′	2.195 (8)
Mo-Cl	2.471 (12)	C_1-N_1	1.158 (11)
Mo-O	1.636 (37)	N_1-C_{11}	1.417 (11)
Mo-C_1	2.132 (8)		
Angles			
O-Mo-Cl	174.0 (1.7)	C_1-Mo-C_1′	91.5 (4)
C_1-Mo-Cl	81.1 (3)	C_1-Mo-C_1″	87.3 (5)
C_1′-Mo-Cl	81.2 (3)	C_1′-Mo-C_1″	162.2 (1)
C_1-Mo-O	94.6 (1.3)	Mo-C_1-N_1	170.2 (8)
C_1′-Mo-O	103.2 (1.3)	C_1-N_1-C_{11}	176.2 (9)

[a] See footnotes *a* and *b* of Table II.

isocyanide carbon atoms. The unit cell packing (Figure 1) accommodates the Mo=O unit on either side of that plane, with chloride on the opposite side, the cation being disordered in the lattice. There are no unusually short intermolecular contacts.

The geometry of the cation (Figure 2) is similar to that found in several related molybdenum(IV)–oxo complexes, selected structural features of which are summarized in Table IV. The mean Mo–C bond length of 2.16 (3) Å compares favorably with those in related molybdenum(IV) cyanide and isocyanide complexes (Table IV and ref 7). It is substantially greater than analogous values in Mo(II) isocyanide complexes,[8,9] as expected.[7] The short Mo–O distance reflects its multiple-bond character.[2] The value of 1.64 ± 0.04 Å is within experimental error (which is large, owing to the disorder) of the Mo–O bond length in the *trans*-oxoaquotetracyanomolybdate(IV) ion.

It is interesting that the Mo–O bond lengths and X–Mo–C angles are correlated, increasing for the series $[MoOCl(CNCH_3)_4]^+ \sim [MoO(OH_2)(CN)_4]^{2-} < [MoO(OH)(CN)_4]^{3-} < [MoO_2(CN)_4]^{4-}$. As the π-donor ability of the trans ligand X increases, oxygen to molybdenum π interactions are weakened at the oxo coordination site, and the metal atom moves toward the plane of the four coordinated carbon atoms (Table IV). A similar correlation holds for the pair of compounds *cis-mer*-$[MoOCl_2L_3]$, L = $P(CH_3)_2(C_6H_5) < P(C_2H_5)_2(C_6H_5)$, where the corresponding Cl–Mo–P or Cl–Mo–Cl angles are compared. Because steric factors in the latter pair of complexes may be important, the absolute values cannot be compared with those for the cyanide and isocyanide complexes.

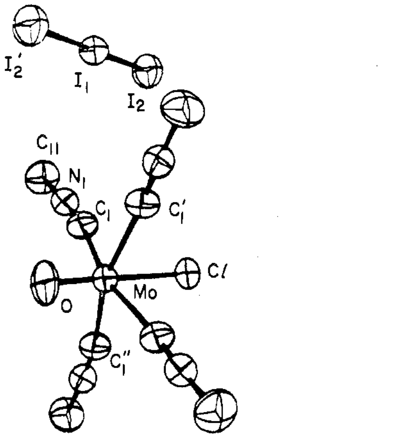

Figure 2. Geometry of the $[MoOCl(CNCH_3)_4]^+$ cation and I_3^- anion showing the atom labeling scheme and 50% probability thermal ellipsoids. The singly primed atoms are related to the unprimed ones by a twofold rotation axis. The O-Mo-Cl moiety lies on a crystallographic mirror plane, which generates C_1'' from C_1.

The Mo–Cl distance in $[MoOCl(CNCH_3)_4]^+$ is ~0.1 Å shorter than the value calculated by adding the difference between the Pauling covalent radii[10] of chlorine (0.99 Å) and oxygen (0.66 Å) to the Mo–OH_2 distance in $[MoO(OH_2)(CN)_4]^{2-}$, perhaps because chloride is a better π donor than water. The value of 2.47 (1) Å for the Mo–Cl bond length agrees well with that found in *trans*-$[MoOCl(diphos)_2]^+$ (Table IV). The geometry of the methyl isocyanide ligands (Table III) is normal. Interbond distances and angles of the linear triiodide ion compare favorably with values in the

Table IV. Comparison of Geometry for Molybdenum(IV)-Oxo Complexes[a]

Complex	Mo-O	Mo-C	Mo-X[b]	X-Mo-C	d[c]	Ref
$[MoOCl(CNCH_3)_4]^+$	1.64 (4)	2.16 (3)	2.471 (12)	81.2 (3)	0.33	This work
$[MoO(OH_2)(CN)_4]^{2-}$	1.668 (5)	2.158 (8)	2.271 (4)	80.9 (3)	0.34	*d*
$[MoO(OH)(CN)_4]^{3-}$	1.698 (7)	2.18 (7)	2.077 (7)	85 (2)	0.21	*d*
	1.72 (1)	2.15 (4)	2.15 (1)	84.0 (7)	0.22	*e*
$[MoO_2(CN)_4]^{4-}$	1.834 (9)	2.205 (15)	1.834 (9)	90.0 (5)	0.0	*f*
$[MoOCl(diphos)_2]^+$	1.69		2.46			*g*
$[MoOCl_2(PMe_2Ph)_3]$	1.676 (7)		2.551 (3)	*h*		*i*
$[MoOCl_2(PEt_2Ph)_3]$	1.801 (9)		2.424 (4)	*j*		*k*

[a] Bond distances are in angstroms and angles in degrees, with standard deviations in parentheses if reported. [b] X ligand trans to oxygen. [c] Distance (Å) of Mo atom from weighted mean plane through four carbon atoms, computed using the published coordinates and the Pippy-Ahmed best-planes program MEAN PLANE. [d] P. R. Robinson, E. O. Schlemper, and R. K. Murmann, *Inorg. Chem.*, **14**, 2035 (1975). [e] K. Stadnicka, *Rocz. Chem.*, 47, 2021 (1973). [f] V. W. Day and J. L. Hoard, *J. Am. Chem. Soc.*, **90**, 3374 (1968). [g] V. C. Adam, U. A. Gregory, and B. T. Kilbourn, *Chem. Commun.*, 1400 (1970). [h] Cl_1-Mo-Cl_2 = 85.5 (1)°, Cl_1-Mo-P_1 = 76.9 (1)°, Cl_1-Mo-P_2 = 89.4 (1)°, and Cl_1-Mo-P_3 = 89.4 (1)°. [i] L. Manojlovic-Muir, *J. Chem. Soc. A*, 2796 (1971). [j] Cl_1-Mo-Cl_2 = 86.4 (2)°, Cl_1-Mo-P_1 = 81.5 (1)°, Cl_1-Mo-P_2 = 90.7 (2)°, and Cl_1-Mo-P_3 = 90.7 (2)°. [k] L. Manojlovic-Muir and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 686 (1972).

literature.[11] Although this ion is often found to be asymmetric, the present structure requires crystallographic $2/m$ site symmetry. It is possible that there is some disorder in the lattice at the triiodide sites, concomitant with the disorder observed for the cation. As noted in the Experimental Section, the final difference Fourier map showed residual electron density in that region. Trial refinements in both centric and acentric space groups were unable to establish this possibility, however.

As discussed previously,[1] the Mo=O stretching bands in the solid-state infrared spectra of $[MoOCl(CNCH_3)_4](I_3)$ and related compounds are split, a result that was ascribed to nonequivalent site symmetries. The present structure is consistent with (but does not prove) that explanation since random disorder of the oxygen and chlorine atoms in the lattice could produce different local environments for the Mo=O oscillator. If the structure were ordered in *Im*, only one Mo=O stretching frequency would be expected.

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Registry No. $[MoOCl(CNCH_3)_4](I_3)$, 50432-36-5.

Supplementary Material Available: Table S1 listing observed and calculated structure factor amplitudes and Table S2 giving root-mean-square amplitudes of thermal vibration (6 pages). Ordering information is given on any current masthead page.

References and Notes

(1) M. Novotny and S. J. Lippard, *Inorg. Chem.*, **13**, 828 (1974).
(2) S. J. Lippard, *Prog. Inorg. Chem.*, **21**, 91 (1976).
(3) J. T. Gill and S. J. Lippard, *Inorg. Chem.*, **14**, 751 (1975).
(4) Calculations were performed on an IBM 360-91 computer. Programs used include FOURIER, a modification by Dellaca and Robinson of the Zalkin program FORDAP; CULS, a local version of the Busing–Martin–Levy structure factor calculation and least-squares refinement program (ORFLS); ORFFE, the Busing–Martin–Levy molecular geometry and error function program; and ORTEP-II, the Johnson thermal ellipsoid plotting program; in addition to various local data processing programs.
(5) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, Tables 2.2A and 2.3.1, pp 72 and 149, respectively.
(6) Supplementary material.
(7) (a) M. Novotny, D. F. Lewis, and S. J. Lippard, *J. Am. Chem. Soc.*, **94**, 6961 (1972); (b) F. H. Cano and D. W. J. Cruickshank, *Chem. Commun.*, 1617 (1971).
(8) (a) D. F. Lewis and S. J. Lippard, *Inorg. Chem.*, **11**, 621 (1972); (b) C. T. Lam, D. L. Lewis, and S. J. Lippard, to be submitted for publication.
(9) D. L. Lewis and S. J. Lippard, *J. Am. Chem. Soc.*, **97**, 2697 (1975).
(10) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960, Table 7-2, p 224.
(11) (a) M. G. B. Drew and J. D. Wilkins, *J. Organomet. Chem.*, **69**, 271 (1974); (b) J. Runsink, S. Swen-Walstra, and T. Migchelsen, *Acta Crystallogr., Sect. B*, **28**, 1331 (1972); (c) J. G. Wijnhoven, Th. E. M. van den Hark, and P. T. Beurskens, *J. Cryst. Mol. Struct.*, **2**, 189 (1972), and references cited therein.

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Two New Compounds in the Ternary System Germanium–Arsenic–Selenium[1]

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In the framework of investigations about crystallization of melts in the ternary system Ge–As–Se we became interested in the preparation of ternary compounds. Vinogradova et al.[2] obtained two crystalline phases by annealing glasses with compositions near Ge:As:Se = 1:1:1. Dta measurements indicated that one was a defined compound at or near the 1:1:1 composition. However, no single-crystal work was reported, probably because it is difficult to prepare crystals of ternary compounds from their melts.

Results and Discussion

Single crystals of GeAsSe and $GeAs_4Se$ (the stoichiometric formulas were determined by electron microprobe analyses) were prepared by a solid–vapor phase reaction of GeSe and As, sealed in evacuated silica ampules, at temperatures between 580 and 600 °C.

When GeSe and As were heated with a 1:1 stoichiometry at 580 °C for 2 h, we obtained only crystals of GeAsSe as reaction product. Two different compounds, GeAsSe and $GeAs_4Se$, resulted when excess arsenic was present in the reaction ampule. Finally, a reaction of GeSe and As with a 1:4 stoichiometry at a temperature of 600 °C for at least 12 h yielded mainly $GeAs_4Se$.

Powder patterns of both compounds were taken. Neither one agreed with those reported by Vinogradova et al.[2] although their data from differential thermal analysis were in agreement with those we took from GeAsSe. Our thermogram of GeAsSe shows a beginning of the melting at a temperature of 617 °C. On cooling (10 °C/min) no exothermic peak due to crystalline solidification was observed. By reheating, a glass transformation step appeared at a temperature of about 400 °C. On further heating, no recrystallization or melting peaks were observed. The thermogram taken of $GeAs_4Se$ shows an endothermic peak beginning at 645 °C (solidus temperature) and a second one ending at 747 °C (liquidus temperature).

Weissenberg and Buerger precession photographs of both compounds were taken. The diffraction symmetry was *mmm* for GeAsSe, and the systematic absences were $0kl$, $k + l = 2n + 1$, $h0l$, $h + 1 = 2n + 1$, and $hk0$, $h = 2n + 1$, consistent with the space group *Pnna* (No. 52). The cell parameters, obtained from x-ray photographs, were $a = 5.07$ Å, $b = 10.12$ Å, and $c = 11.69$ Å with $Z = 8$. For $GeAs_4Se$ the diffraction symmetry was $2/m$ and the systematic absences were $00l$, $l = 2n + 1$, indicating the space groups $P2_1$ (No. 4) or $P2_1/m$ (No. 11). The cell parameters, also obtained from film data, were $a = 12.37$ Å, $b = 6.57$ Å, $c = 3.59$ Å, and $\gamma = 101°$ with $Z = 2$.

The compound GeAsSe seems to have a marked tendency to twin which made it difficult to find single crystals of a quality suitable for x-ray measurements. Another difficulty arises from the mechanical properties of both compounds. GeAsSe crystallizes as platelets, which show a distinct sheet splitting. These platelets are highly sensitive to mechanical deformations, and when touched, they very easily bend plastically. $GeAs_4Se$ crystallizes as thin "laths", which show an extreme fiber splitting when stressed.

The optical properties also help to distinguish the two compounds. $GeAs_4Se$ is opaque and a grayish and has a metallic shine in reflecting light. GeAsSe also has a metallic luster in reflecting light but appears red in transmitting light. If polarized light is transmitted perpendicularly to the plane of the platelet, the optical properties of GeAsSe are in agreement with the symmetry proposed.

Registry No. GeSe, 12065-10-0; As, 7440-38-2; GeAsSe, 12344-64-8; $GeAs_4Se$, 58228-76-5.

References and Notes

(1) This research was supported by the Deutsche Forschungsgemeinschaft (DFG).
(2) G. Z. Vinogradova, S. A. Dembovskij, and N. P. Luzhnaya, *Zh. Neorg. Chim.*, **13**, 1444 (1968).