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Synthesis and Crystal and Molecular Structure of *cis*-Dioxodichloro[diisopropyl (*N*,*N*-diethylcarbamyl)methylenephosphonate]molybdenum(VI)

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cis-Dioxodichloro[diisopropyl (*N*,*N*-diethylcarbamyl)methylenephosphonate]molybdenum(VI), $MoO_2Cl_2[(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2]$, has been prepared from the addition of MoO_2Cl_2 to the phosphonate ligand in ethanol. The resulting complex has been characterized by infrared and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and single-crystal X-ray diffraction analysis. The complex was found to crystallize in the monoclinic space group $P2_1/c$ with $a = 13.829$ (3) Å, $b = 8.824$ (2) Å, $c = 16.647$ (4) Å, $\beta = 90.61$ (2)°, $Z = 4$, $V = 2031.2$ (9) Å^3, and $\rho_{calcd} = 1.56$ g cm^{-3}. The structure was solved by heavy-atom techniques, and blocked least-squares refinement converged with $R_F = 3.3\%$ and $R_{wF} = 3.4\%$ for 3502 unique reflections with $F \geq 5\sigma(F)$. The structure contains monomeric units of the complex with the six-coordinate Mo atom having a pseudooctahedral coordination geometry. The carbamylmethylenephosphonate ligand is bonded to the Mo atom in a bidentate manner. Several important bond distances are Mo–O(oxo)$_{av}$ = 1.683 (2) Å, Mo–Cl$_{av}$ = 2.380 (1) Å, Mo–O(phosphoryl) = 2.220 Å, Mo–O(carbonyl) = 2.246 (2) Å, P=O = 1.487 (2) Å, and C=O = 1.262 (3) Å.

Introduction

Carbamylmethylenephosphonates, $(RO)_2P(O)CH_2C(O)NR_2$ (CMP), and carbamylphosphonates, $(RO)_2P(O)C(O)NR_2$ (CP), are known to be effective extractants for lanthanide (Ln) and actinide (An) ions present in acidic nuclear waste solutions.[1-3] In an effort to reveal in greater detail how these extractants effect selective metal ion separations, we have isolated and structurally characterized a number of Ln and An complexes containing CMP ligands.[4-7] These studies and complementary solution equilibrium analyses performed by Horwitz and co-workers[8-14] have confirmed that the molecular operation of CMP ligands as metal ion extractants is indeed complex and interesting.

A limited number of transition metals including Y, Zr, Tc, Pd, Nb, Ru, and Mo also are extracted by CMP and CP ligands,[2,3,15] and there exists considerable potential for new separation schemes involving these metals and extractants. Despite interest in this area, little is known regarding extraction mechanisms or the stoichiometries and structures of the extraction complexes. McIsaac and Baker[16,17] have examined extraction equilibria between $(C_6H_{13}O)_2P(O)CH_2C(O)N(C_2H_5)_2$ (DHDECMP) and Zr(IV), Pd(II), and TcO_4^- in nitric acid, and they have proposed the formation of $Zr(NO_3)_4(DHDECMP)_2$, $HTcO_4(DHDECMP)_3$, and $Pd(NO_3)_2(DHDECMP)_3$ in solution.[18] At this time only one related complex, $Pd(NO_3)_2$(DiPDECMP), has been isolated and structurally characterized.[19,20] On the basis of this structure determination, it appears that the isolated complex carries fewer CMP ligands than the number proposed from solution extractant dependency measurements. This feature has been observed in each of the isolated and structurally characterized Ln– and An–CMP complexes,[4-7] and as yet a complete justification for this observation has not been unambiguously forwarded.

As part of our continuing studies of the molecular mechanics of metal ion extractions, we have investigated the interactions of several CMP ligands with Mo(VI), and we report here on the preparation, isolation, and characterization of $MoO_2Cl_2[(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2]$ (**1**).

Table I. Experimental Data for the X-ray Diffraction Study of $MoO_2Cl_2[(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2]$

(A) Crystal Parameters at 23 °C

cryst syst: monoclinic	mol wt = 478.2
space group: $P2_1/c$	$V = 2031.2$ Å^3
$a = 13.829$ (3) Å	$\rho_{calcd} = 1.563$ g cm^{-3}
$b = 8.824$ (2) Å	$\rho_{obsd} = 1.564$ g cm^{-3}
$c = 16.647$ (4) Å	$\mu = 10.0$ cm^{-1}
$\beta = 90.61$ (2)°	$F(000) = 976$
$Z = 4$	

(B) Data Collection

diffractometer: Syntex P3/F
radiation: Mo Kα ($\bar{\lambda} = 0.710\,69$ Å)
monochromator: highly oriented graphite cryst
reflcns measd: $\pm h, \pm k, +l$
2θ range: 1-55°
scan type: Ω
scan speed: 5.9-29.3° min^{-1}
scan range: $(\omega_0 - 0.9)°-(\omega_0 + 0.9)°$
bkgd measmt: stationary cryst and counter; at the beginning and end of Ω scan, each for half the total Ω scan time
std reflcns: 3 measd every 141 reflcns [10,0,0, 0,6,0, 0,0,10]; no signif changes in intens obsd
unique reflcns collected: 4669
obsd reflcns used in refinement: 3502 with $F \geq 5\sigma(F)$
weighting scheme: $1/[\sigma(F)^2 + gF^2]$, $g = 0.000\,30$
no. of parameters: 208

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(1) Siddall, T. H. *J. Inorg. Nucl. Chem.* **1963**, *25*, 883; **1964**, *26*, 1991.
(2) Schulz, W. W.; McIsaac, L. D. "Transplutonium Elements"; Müller, W., Lindner, R., Eds.; North-Holland Publishing Co.: Amsterdam, 1976; p 433.
(3) Schulz, W. W.; McIsaac, L. D. "Recent Developments in Separation Science"; Li, N. N., Ed.; CRC Press: Boca Raton, FL, 1982; Vol. VII, p 31.
(4) Bowen, S. M.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **1982**, *21*, 261.
(5) Bowen, S. M.; Duesler, E. N.; Paine, R. T. *Inorg. Chim. Acta* **1982**, *61*, 155.
(6) Bowen, S. M.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **1983**, *22*, 286.
(7) Bowen, S. M.; Duesler, E. N.; Paine, R. T. *Inorg. Chim. Acta* **1984**, *84*, 221.
(8) Horwitz, E. P.; Kalina, D. G.; Muscatello, A. C. *Sep. Sci. Technol.* **1981**, *16*, 403.
(9) Horwitz, E. P.; Muscatello, A. C.; Kalina, D. G.; Kaplan, L. *Sep. Sci. Technol.* **1981**, *16*, 417.
(10) Kalina, D. G.; Mason, G. W.; Horwitz, E. P. *J. Inorg. Nucl. Chem.* **1981** *43*, 159.
(11) Kalina, D. G.; Horwitz, E. P.; Kaplan, L.; Muscatello, A. C. *Sep. Sci. Technol.* **1981**, *16*, 1127.
(12) Muscatello, A. C.; Horwitz, E. P.; Kalina, D. G.; Kaplan, L. *Sep. Sci. Technol.* **1982**, *17*, 859.
(13) Horwitz, E. P.; Diamond, H.; Kalina, D. G. "Plutonium Chemistry"; American Chemical Society: Washington, DC, 1982; ACS *Symp.* Ser. No. 216.
(14) Danesi, P. R.; Horwitz, E. P.; Rickert, P. G. *J. Phys. Chem.* **1983**, *87*, 4708.
(15) Aly, H. F.; Kandil, A. H. T.; Raieh, M. *Fresenius' Z. Anal. Chem.* **1972**, *258*, 281.
(16) McIsaac, L. D.; Baker, J. D. *Solvent Extr. Ion Exch.* **1983**, *1*, 27.
(17) McIsaac, L. D. *Sep. Sci. Technol.* **1983**, *17*, 387.
(18) The following abbreviations have been used in the text: DHDECMP = $(C_6H_{13}O)_2P(O)CH_2C(O)N(C_2H_5)_2$; DiPDECMP = $(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2$; DEDECMP = $(C_2H_5O)_2P(O)CH_2C(O)N(C_2H_5)_2$.
(19) Jessup, J. J.; Duesler, E. N.; Paine, R. T. *Inorg. Chim. Acta* **1983**, *73*, 261.
(20) A complex $HReO_4$(DEDECMP) has been isolated and characterized; however, the molecular structure has not been determined by single-crystal X-ray crystallography. Paine, R. T., unpublished results.

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Experimental Section

General Information. $(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2$, DiPDECMP, was prepared by literature methods.[1] MoO_2Cl_2 was obtained from Alfa Products (Ventron). Infrared spectra were recorded on a Perkin-Elmer Model 621 infrared spectrometer. The samples were prepared as KBr pellets, and the spectra were calibrated with standard absorptions from a polystyrene film. The NMR spectra were recorded on a Varian FT-80 NMR spectrometer operating at 32.2 MHz (^{31}P), 20.0 MHz (^{13}C), and 80.0 MHz (^1H). The samples, dissolved in an internal deuterium lock solvent for the ^{13}C and ^1H spectra, were contained in 5-mm tubes. An external deuterium lock solvent in a 10-mm tube was used for the ^{31}P spectra. Spectral standards were 85% H_3PO_4 (^{31}P) and Me_4Si (^{13}C and ^1H).

Preparation of 1. The complex $MoO_2Cl_2[(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2]$ (**1**) was prepared by addition of 4.5 mmol of MoO_2Cl_2 to 9.0 mmol of DiPDECMP in ethanol. The resulting blue solution was allowed to evaporate. During solvent evaporation the solution was observed to change to a yellow color after 24 h and to a blue-green color after 72 h. Crystalline material formed after 96 h, which was collected by filtratrion and washed with diethyl ether. Recrystallization from benzene resulted in a light blue-green solid containing crystals suitable for X-ray diffraction analysis. Anal. Calcd for $MoO_6Cl_2PNC_{12}H_{26}$: C, 30.14; H, 5.48; N, 2.93. Found: C, 30.34; H, 5.66; N, 3.04. Infrared spectrum (cm^{-1}, KBr pellet): 1596 (ν_{CO}, s), 1193 (ν_{PO}, m); 1168 (ν_{PO}, m), 1008 (ν_{POC}, s), 950 ($\nu_{MoO}{}^{sym}$, m), 909 ($\nu_{MoO}{}^{asym}$, m). NMR spectra (27 °C): $^{31}P\{^1H\}$ (D_2O solvent) δ 23.3; $^{13}C\{^1H\}$ (C_6H_6/C_6D_6 solvent) δ 166.7 ($^2J_{PC(2)} = 4.8$ Hz, C=O), 75.0 ($^2J_{PC(7)} = 6.1$ Hz, $\mathit{C}H(CH_3)_2$), 44.3 (NCH_2), 43.0 (NCH_2), 28.7 ($^1J_{Pc(1)} = 139.6$ Hz, $P\mathit{C}H_2C$), 23.4 ($\mathit{C}H_3CH_2O$), 13.8 ($\mathit{C}H_3CH_2N$), 12.8 ($\mathit{C}H_3CH_2N$); ^1H (C_6H_6/C_6D_6 solvent) δ 5.03 (CHO, 2 H), 3.18 ($^1J_{PH} = 22.4$ Hz, PCH_2C, 2 H)), 3.14 (NCH_2, 4 H), 1.24 ($NCH_2\mathit{CH}_3$, 6 H), 1.00 (OCH_2CH_3 (12 H)). The crystalline solid is soluble in benzene, ethanol, chloroform, water, and acetone, and it is air stable.

Crystal Structure Determination. A crystal suitable for X-ray diffraction analysis (0.61 mm × 0.39 mm × 0.07 mm) was glued to the end of a glass fiber. The crystal was centered on a Syntex P3/F automated diffractometer, and determinations of the crystal class, orientation matrix, and unit cell dimensions were performed in a standard manner.[4] Data were collected at 23 °C in the Ω scan mode using Mo Kα radiation, a scintillation counter, and a pulse height analyzer. The data collection parameters are summarized in Table I. Collected data were consistent with the monoclinic space group $P2_1/c$. Corrections for absorption were made empirically on the basis of ψ scans, and the maximum and minimum transmission factors were 0.465 and 0.422. Redundant and equivalent reflection data were averaged and converted to unscaled $|F_o|$ values after corrections for Lorentz and polarization effects.

Solution and Refinement of the Structure. Calculations were performed with the R3/SHELXTL structure determination package.[21] Anomalous dispersion terms were included for atoms with $Z > 2$. Least-squares refinement in this package uses a blocked-cascade algorithm with full-matrix blocks of 103 parameters.[22] The solution and refinement of the strucure were based on 3502 reflections with $F \geq 5\sigma(F)$. The molybdenum atom was located by Patterson methods. Sixteen other atoms were located by phasing on the molybdenum atom. Two cycles of least-squares refinement located the remaining non-hydrogen atoms. Refinement of the positional and isotropic thermal parameters gave $R_F = 10.8\%$. Application of individual anisotropic thermal parameters to all non-hydrogen atoms gave $R_F = 4.4\%$. All hydrogen atoms were located in fixed idealized positions and their isotropic thermal parameters varied. Final least-squares refinement gave $R_F = 3.3\%$ and $R_{wF} = 3.4\%$. A final difference map showed the first six peaks (0.98–0.74 e $Å^{-3}$) to be ≤1.09 Å from the Mo, O(1), and C(12) atoms. The seventh peak (0.62 e $Å^{-3}$) is 0.89 Å from the P atom, and the remaining peaks are ≤0.59 e $Å^{-3}$. The observed and calculated structure factor amplitudes (Table S-1), hydrogen atom positions (Table S-2), and anisotropic thermal parameters (Table S-3) are available in the supplementary material. The non-hydrogen atom positional parameters are listed in Table II.

Table II. Fractional Coordinates and Their Esd's for $MoO_2Cl_2[(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2]$

atom	x	y	z
Mo	0.21950 (2)	0.13619 (3)	0.14040 (1)
Cl(1)	0.35975 (7)	0.29179 (12)	0.14252 (5)
Cl(2)	0.07989 (7)	0.00094 (13)	0.09531 (5)
P(1)	0.26252 (5)	0.10280 (9)	−0.06170 (4)
O(A)	0.1638 (2)	0.2260 (3)	0.2165 (1)
O(B)	0.2702 (2)	−0.0138 (3)	0.1861 (1)
O(1)	0.2806 (2)	0.0628 (2)	0.0239 (1)
O(2)	0.3365 (2)	0.2133 (3)	−0.0993 (1)
O(3)	0.2579 (2)	−0.0443 (2)	−0.1127 (1)
O(4)	0.1620 (2)	0.3168 (2)	0.0577 (1)
N(1)	0.1492 (2)	0.4801 (3)	−0.0444 (1)
C(1)	0.1518 (2)	0.2059 (3)	−0.0726 (2)
C(2)	0.1543 (2)	0.3400 (3)	−0.0169 (2)
C(3)	0.1507 (2)	0.5191 (4)	−0.1309 (2)
C(4)	0.0505 (3)	0.5300 (5)	−0.1674 (2)
C(5)	0.1497 (3)	0.6086 (4)	0.0119 (2)
C(6)	0.2510 (3)	0.6597 (4)	0.0328 (2)
C(7)	0.4363 (3)	0.2457 (5)	−0.0744 (3)
C(8)	0.5009 (3)	0.1283 (7)	−0.1067 (4)
C(9)	0.4569 (4)	0.4008 (6)	−0.1049 (4)
C(10)	0.2691 (3)	−0.0487 (4)	−0.2012 (2)
C(11)	0.3449 (3)	−0.1620 (5)	−0.2190 (3)
C(12)	0.1726 (3)	−0.0860 (5)	−0.2380 (3)

Results and Discussion

A blue-green solid (**1**) results from the combination of diisopropyl (*N*,*N*-diethylcarbamyl)methylenephosphonate (DiPDECMP) and MoO_2Cl_2 in ethanol in a 2:1 mole ratio. Elemental analysis is consistent with the formation of only a 1:1 complex as indicated in[23]

$$\text{DiPDECMP} + MoO_2Cl_2 \xrightarrow{\text{EtOH}} MoO_2Cl_2(\text{DiPDECMP})$$

The infrared spectrum of **1** obtained from a KBr pellet displays a strong absorption at 1596 cm^{-1} and a split band[24] at 1193 and 1168 cm^{-1}, which can be assigned to ν_{CO} and ν_{PO}, respectively. These absorptions compared with the uncoordinated ligand infrared bands at 1648 and 1253 cm^{-1}, and the down-frequency shifts, $\Delta\nu_{CO} = 52$ cm^{-1} and $\Delta\nu_{PO} = 60\text{–}85$ cm^{-1}, are comparable to those shifts observed in CMP coordination complexes with UO_2^{2+},[6] Th(IV),[4] and early lanthanides.[5] In these complexes the large down-frequency shifts for solid samples were confirmed to be diagnostic of bidentate CMP coordination to the central metal atom by single-crystal X-ray analyses. Coordination of the monodentate ligand Ph_3PO with MoO_2X_2 (X = F, Cl, Br) results in down-frequency ν_{PO} shifts, $\Delta\nu_{PO} = 41\text{–}55$ cm^{-1},[26] and single-crystal X-ray structure determinations verified the phosphoryl oxygen atom binding to the MoO_2^{2+} unit. The dioxomolybdenum terminal oxygen symmetric and asymmetric stretches are tentatively assigned to bands at 950 and 909 cm^{-1}, respectively. These absorptions can be compared to bands found in several related complexes: $MoO_2Cl_2[HC(O)N(C_2H_5)_2]_2$, 940 and 905 cm^{-1};[27] MoO_2Cl_2(2,2′-bpy), 938 and 904 cm^{-1},[27] and $MoO_2Cl_2[Ph_3PO]_2$, 947 and 905 cm^{-1}.[26] On the basis of these data a cis-trans-cis octahedral arrangement of the terminal oxygen atoms, chlorine atoms, and CMP ligand CO and PO oxygen atoms in **1** can be assumed.

The $^{31}P\{^1H\}$ NMR spectrum of **1** displays a singlet at 23.3 ppm, which is slightly downfield of the uncoordinated DiPDECMP resonance at 22.0 ppm. Similar small downfield shifts, and in some cases upfield coordination shifts, have been found in UO_2^{2+}–,[6] Th(IV)–,[4] and lanthanide–CMP[5] complexes, as well as for a number of other metal–phosphoryl ligand complexes.[28,29] The

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(21) Sheldrick, G. M. "Nicolet SHELXTL Operations Manual"; Nicolet XRD Corp.: Cupertino, CA, 1981. SHELXTL uses scattering factors compiled in: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1968; Vol. IV.

(22) A general description of the least-squares algebra is found in: Ahmed, F. R., Hall, S. R., Huber, C. P., Eds. "Crystallographic Computing"; Munksgaard Publishing Co.: Copenhagen, 1970; p 187.

(23) An identical complex is formed in aqueous solutions.

(24) Split ν_{PO} and ν_{CO} bands have been observed in the infrared spectra of several metal–CMP complexes;[4,25] however, a full understanding of the splitting has not been realized.

(25) Stewart, W. E.; Siddal, T. H. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3599. Stewart, W. E.; Siddall, T. H. *J. Inorg. Nucl. Chem.* **1968**, *30*, 3281.

(26) Butcher, R. J.; Penfold, B. R.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1979**, 688.

(27) Butcher, R. J.; Gunz, H. P.; Maclagan, R. G. A. R.; Powell, H. K. J.; Wilkins, C. J.; Hian, Y. S. *J. Chem. Soc., Dalton Trans.* **1975**, 1223.

(28) Mark, V.; Dungan, D.; Crutchfield, M.; Van Wazer, J. *Top. Phosphorus Chem.* **1967**, *5*, 1.

Table III. Selected Interatomic Distances (Å)

Mo-O(A)	1.687 (2)	C(7)-C(8)	1.473 (7)
Mo-O(B)	1.677 (2)	C(7)-C(9)	1.488 (7)
Mo-Cl(1)	2.376 (1)	C(10)-C(11)	1.481 (6)
Mo-Cl(2)	2.384 (1)	C(10)-C(12)	1.499 (6)
Mo-O(1)	2.220 (2)	C(1)-C(2)	1.503 (4)
Mo-O(4)	2.246 (2)	C(2)-O(4)	1.262 (3)
P(1)-O(1)	1.487 (2)	C(2)-N(1)	1.320 (4)
P(1)-O(2)	1.550 (2)	N(1)-C(3)	1.481 (4)
P(1)-O(3)	1.552 (2)	N(1)-C(5)	1.471 (4)
P(1)-C(1)	1.788 (3)	C(3)-C(4)	1.509 (5)
O(2)-C(7)	1.465 (4)	C(5)-C(6)	1.508 (6)
O(3)-C(10)	1.483 (4)		

Table IV. Selected Interatomic Bond Angles (deg)

O(A)-Mo-O(B)	102.8 (1)	Cl(2)-Mo-O(4)	83.2 (1)
Cl(1)-Mo-Cl(2)	162.2 (1)	Mo-O(4)-C(2)	138.1 (2)
O(1)-Mo-O(4)	78.9 (1)	Mo-O(1)-P(1)	135.0 (1)
O(A)-Mo-O(1)	166.8 (1)	O(1)-P(1)-O(2)	115.6 (1)
O(A)-Mo-O(4)	88.0 (1)	O(1)-P(1)-O(3)	109.4 (1)
O(A)-Mo-Cl(1)	95.6 (1)	O(2)-P(1)-O(3)	109.2 (1)
O(A)-Mo-Cl(2)	95.5 (1)	O(1)-P(1)-C(1)	110.7 (1)
O(B)-Mo-O(1)	90.3 (1)	O(2)-P(1)-C(1)	101.9 (1)
O(B)-Mo-O(4)	169.1 (1)	O(3)-P(1)-C(1)	109.9 (1)
O(B)-Mo-Cl(1)	96.5 (1)	O(4)-C(2)-C(1)	118.7 (3)
O(B)-Mo-Cl(2)	94.6 (1)	N(1)-C(2)-O(4)	119.8 (3)
Cl(1)-Mo-O(1)	82.2 (1)	N(1)-C(2)-C(1)	121.5 (3)
Cl(1)-Mo-O(4)	83.3 (1)	P(1)-C(1)-C(2)	108.9 (2)
Cl(2)-Mo-O(1)	83.9 (1)		

$^{13}C\{^1H\}$ shifts for the central methylene group ($P(O)CH_2C(O)$) and the carbonyl group of **1**, 28.7 ppm (J_{PC} = 139.6 Hz) and 166.7 ppm (J_{PC} = 4.8 Hz), and other metal–CMP complexes, might be expected to provide additional detail regarding the structures of the complexes. With other diamagnetic complexes containing bidentate CMP ligands a small upfield methylene carbon shift and increased P–C coupling constant is found compared to those for the uncoordinated ligand, 34.8 ppm (J_{PC} = 133.6 Hz). This trend is observed in **1**; however, the coupling constant shift upon coordination is smaller than that observed in the related UO_2^{2+}, Th(IV), and lanthanide complexes reported previously.[4-6] Unfortunately, no clear trend has emerged for ^{13}C shifts of coordinated carbonyl groups in these complexes since both small positive and negative changes in chemical shifts are observed. It is noteworthy that the ^{13}C and ^1H NMR data for **1** show two chemically inequivalent amide alkyl groups, which indicate that free rotation about the (O)C–N(*i*-Pr) bond is restricted in the complex.

A single-crystal X-ray diffraction structure determination for **1** was undertaken, and this analysis confirms the 1:1 metal–CMP ligand stoichiometry and the bidentate ligand–metal interaction. The structure contains discrete monomeric units of formula MoO_2Cl_2(DiPDECMP) with four molecules per unit cell. A view of the molecule is shown in Figure 1, and selected bond distances and angles are summarized in Tables III and IV.

The Mo(VI) atom is bonded to two terminal oxygen atoms, two terminal chlorine atoms, and the phosphoryl and carbonyl oxygen atoms of a bidentate DiPDECMP ligand. These nearest-neighbor atoms form an approximately octahedral arrangement. The terminal oxygen atoms are cis to each other while the chlorine atoms are trans to each other. Related coordination geometries have been found in $MoO_2Cl_2[Ph_3PO]_2$ (**2**),[26] MoO_2Cl_2(9,10-phenquin) (**3**, 9,10-phenquin = 9,10-phenanthrenequinone),[30] $MoO_2Cl_2(DMF)_2$ (**4**, DMF = *N,N*-dimethylformamide),[31] and MoO_2Cl_2(*o*-phen) (**5**, *o*-phen = *o*-phenanthroline).[32] The molybdenum-terminal oxygen atom distances in **1**, Mo–O(A) = 1.687 (2) Å and Mo–O(B) = 1.677 (2) Å, are comparable to those related distances in **2** (1.695 (1) and 1.673 (1) Å), **3** (1.671 (3) Å), **4**, (1.68 (1) Å), **5** (1.695 (3) Å), $MoO_2Cl_2[Cl_3PO]$ (**6**)[33] (1.689 (4)$_{av}$ Å), and $MoO_2(HOCH_2CH_2O)$ (**7**)[34] (1.723 (10) Å (average)). These interactions may be assumed to have double-bond character.[35] The O(A)–Mo–O(B) angle, 102.8 (1)°, is also comparable with the related angles in **2** (103.17 (7)°), **3** (104.8 (2)°), **4** (102.2 (7)°), **5** (106.8 (2)°), **6** (103.1 (2) and 102.9 (2)°), and **7** (107.6 (5) and 104.6 (5)°). The Mo–Cl bond distances and Cl(1)–Mo–Cl(2) bond angle in **1**, Mo–Cl(1) = 2.376 (1) Å, Mo–Cl(2) = 2.384 (1) Å, and Cl(1)–Mo–Cl(2) = 162.2 (1)°, compare with distances and angles in **2** (2.397 (1) and 2.388 (1) Å and 164.62 (5)°), **3** (2.370 (3) and 2.343 (3) Å and 156.3 (1)°), **4** (2.341 (7) Å and 161.3 (2)°), **5** (2.361 (1) Å and 157.71 (5)°), and **6** (2.297 (2)–2.321 (2) Å and 155.92 (6)° (average)).

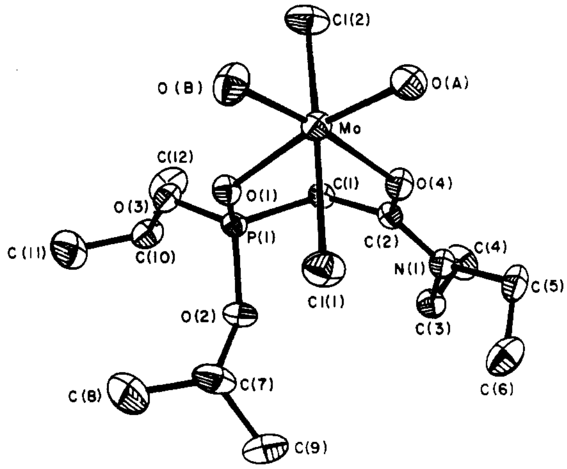

Figure 1. Molecular geometry and atom-labeling scheme for $MoO_2Cl_2[(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2]$ (25% probability ellipsoids).

The molybdenum-phosphoryl oxygen atom bond distance in **1**, Mo–O(1) = 2.220 (2) Å, is similar to those found in the Ph_3PO complex **2** (2.17 (1) and 2.19 (1) Å), but it is significantly shorter than the distances in the Cl_3PO complex **6** (2.329 (4) and 2.328 (4) Å). The molybdenum–carbonyl oxygen atom bond distance in **1**, Mo–O(4) = 2.246 (2) Å, can be compared with related distances in **3** (2.305 (3) and 2.306 (3) Å), **4** (2.20 (1) Å), and **7** (2.142 (9) Å). The O(1)–Mo–O(4) "bite" angle in **1**, 78.9 (1)°, is similar to the corresponding angles in **2** (77.81 (5)°) and **4** (76.2 (5)°), which contain two monodentate ligands, and larger than the angles in **3** (68.5 (1)°) and **7** (74.6 (3)°), which contain bidentate oxygen donating ligands. On the basis of these angles, it appears that DiPDECMP bidentate coordination does not impose strain in the resulting chelate ring.

It is interesting to note that the short terminal Mo–O distance, Mo–O(B), is trans to the longer Mo–O(ligand) distance, Mo–O(4), associated with the carbonyl group and the long terminal Mo–O distance, Mo–O(A), is trans to the shorter Mo–O(1) distance associated with the phosphoryl group. These distances might be interpreted to suggest that the carbonyl oxygen atom functions as a weaker base site compared to the phosphoryl oxygen atom, which would be consistent with solution protonation equilibria found for CMP ligands.[36] In the uranyl complex $UO_2(NO_3)_2$(DiPDECMP),[6] the terminal oxygen atoms are, of course, trans to each other and cis to the carbonyl and phosphoryl oxygen atoms. It is found that the UO(P) distance 2.420 (4) Å, is slightly longer than the U–O(C) distance, 2.406 (5) Å. Clearly, care must be taken in assuming relative base strengths of ligand

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(29) DeBolster, M. W. G.; Groeneveld, W. L. *Top. Phosphorus Chem.* **1976**, *8*, 273.

(30) Pierpont, C. G.; Downs, H. H. *Inorg. Chem.* **1977**, *16*, 2970.

(31) Florian, L. R.; Corey, E. R. *Inorg. Chem.* **1968**, *7*, 722.

(32) Viossat, B.; Rodier, N. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 2715.

(33) Beyendorff-Gulba, G.; Strähle, J.; Liebelt, A.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1981**, *483*, 26.

(34) Schröder, F. A.; Scherle, J.; Hazell, R. G., *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 531.

(35) Schröder, F. A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 2294.

(36) Paine, R. T.; Jessup, J. J.; McCabe, D. J., unpublished results.

coordination sites based solely on coordination bond distances.

The bond distances and angles associated with the coordinated DiPDECMP ligand in **1** are typical of those found in $UO_2(NO_3)_2$(DiPDECMP) (**8**), $Th(NO_3)_4$(DEDECMP)$_2$ (**9**), and $Sm(NO_3)_3$(DiPDECMP)$_2$ (**10**). The phosphoryl bond distance P(1)–O(1), 1.487 (2) Å, compares with distances in **8** (1.485 (5) Å), **9** (1.478 (4) Å), and **10** (1.480 (2) Å) as well as with the distances in the monodentate phosphoryl complex **2** (1.492 (1) Å). The corresponding distances in **6** are much shorter: 1.457 (4) and 1.437 (4) Å. The carbonyl bond distance C(2)–O(4), 1.262 (3) Å, in **1** is also similar to those found in **8** (1.260 (8) Å), **9** (1.256 (6) Å), and **10** (1.261 (3) Å). The corresponding distances in other Mo(VI)–carbonyl complexes show greater variability: **3**, 1.233 (4) Å and 1.235 (4) Å; **4**, 1.29 (1) Å. The bond angles about P(1), C(1), and C(2) compare well with the angles found in **8**, **9**, and **10**.

The isolation, characterization, and single-crystal X-ray structure determination for **1** indicate that in the solid state this complex contains a single DiPDECMP ligand bonded in a cis-bidentate configuration to MoO_2Cl_2. The composition and structure of the species formed in solution during the extraction of MoO_2Cl_2 by CMP ligands are under investigation in our group at this time.

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Supplementary Material Available: Listings of structure factors, hydrogen atom positional parameters, and thermal parameters (13 pages). Ordering information is given on any current masthead page.

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Crystal Structures and Magnetic and EPR Studies of Intradimer and Interdimer Exchange Coupling in $[M(en)_3]_2[Cu_2Cl_8]Cl_2\cdot 2H_2O$ (M = Co, Rh, Ir) Crystals

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Single-crystal EPR measurements and magnetic susceptibility data are presented for the compounds $[M(C_2H_8N_2)_3]_2[Cu_2Cl_8]Cl_2\cdot 2H_2O$ (M = Co (I), Rh (II), Ir (III); $C_2H_8N_2$ = ethylenediamine, en). The crystal and molecular structures of $[M(en)_3]_2[Cu_2Cl_8]Cl_2\cdot 2H_2O$ (M = Rh (II), Ir (III)) have been determined from single-crystal, three-dimensional X-ray diffraction counter data. The compounds crystallize as orange prisms in space group *Pbca* with $Z = 4$ and have unit cell dimensions of $a = 13.639$ (6) Å, $b = 14.577$ (11) Å, and $c = 18.020$ (6) Å for the rhodium compound and $a = 13.705$ (5) Å, $b = 14.467$ (19) Å, and $c = 18.091$ (6) Å for the iridium compound. The structures were refined by full-matrix least-squares techniques to *R* values of 0.036 for the rhodium compound and 0.049 for the iridium compound. The compounds are isomorphous with $[Co(en)_3]_2[Cu_2Cl_8]Cl_2\cdot 2H_2O$. The crystal structure consists of layers of magnetically inequivalent $Cu_2Cl_8^{4-}$ dimers with antiferromagnetic intradimer coupling $2J = -14.6$ cm^{-1} in I, -13.8 cm^{-1} in II, and -13.0 cm^{-1} in III. The dimers are well separated by large $[M(en)_3]^{3+}$ diamagnetic complexes. The hyperfine and fine structures are not resolved in the EPR spectra. The spectra are partially averaged by interdimer exchange interaction and indicate a strong merging effect of the EPR lines. The EPR spectral parameters were determined by computer simulation using solutions to the generalized Bloch equations. Molecular *g* factors have been found to be similar in all three compounds with $g_z = 2.290$, $g_y = 2.020$, and $g_x = 2.116$ in II. From the simulation procedure the values of the interdimer exchange integrals between neighbor layers have been found to be 0.007 12 cm^{-1} in I, 0.001 35 cm^{-1} in II, and 0.001 90 cm^{-1} in III at room temperature. This weak exchange coupling decreases linearly with temperature and reaches values of 0.003 14 cm^{-1} in I, 0.000 70 cm^{-1} in II, and 0.000 52 cm^{-1} in III at 77 K. This is a result of decreases in overlaps between atomic orbitals in the superexchange pathways with decreases of the average amplitudes of thermal lattice vibrations.

Introduction

Magnetostructural correlations in hydroxo-bridged,[2,3] alkoxo-bridged,[4] chloro-bridged,[5,6] bromo-bridged,[6] and sulfur-bridged[6,7] copper(II) dimers are well documented experimentally. The dimeric unit $[Cu_2Cl_8]^{4-}$ in $[Co(en)_3]_2[Cu_2Cl_8]Cl_2\cdot 2H_2O$ obeys the predicted[5,6] relationship between singlet–triplet splitting $2J$ and the quotient ϕ/R_0 (ϕ = bridge angle, R_0 = longest bridge arm) with $2J = -14.6$ cm^{-1} [7] and $\phi/R_0 = 35.2°$ Å^{-1}.[8,9] The $2J$, ϕ/R_0 dependence is very sensitive to small changes in the bridge geometry. Thus, a substitution for the Co(III) ion in $[Co(en)_3]_2[Cu_2Cl_8]Cl_2\cdot 2H_2O$ by ions with larger ionic radii, such as Rh(III) or Ir(III), should result in small changes in ϕ/R_0 from the influence of the size of the cation on the crystal packing.

We have previously reported[9] the crystal structure of $[Co(en)_3]_2[Cu_2Cl_8]Cl_2\cdot 2H_2O$, and the structures of the Rh(III) and Ir(III) complexes are shown here to be isomorphous. EPR powder spectra of the compounds, recorded at both room temperature and 77 K, are unusual since absorptions appear from both averaged and nonaveraged EPR lines of magnetically nonequivalent copper(II) complexes in the unit cell. This observation strongly suggests an interdimer interaction with a coupling strength in the range that can be observed by EPR spectroscopy. The EPR lines from nonequivalent complexes are perturbed by this interaction, and EPR spectral parameters cannot be determined directly from recorded EPR spectra. The interpretation of the EPR spectra of $[Co(en)_3]_2[Cu_2Cl_8]Cl_2\cdot 2H_2O$[10–12] has been refined to take this effect into account, and the spectra of the Rh(III) and Ir(III) analogues are also presented and interpreted in terms of temperature-dependent interdimer interactions.

Experimental Section

Electron Paramagnetic Resonance. EPR spectra were recorded with a Varian E-109 spectrometer at X-band. The microwave frequency was monitored with a Hewlett-Packard 5245L frequency counter, and the

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[2] Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107.

[3] Hatfield, W. E. In "Theory and Applications of Molecular Paramagnetism"; Boudreaux, E. A., Mulay, L. N., Eds.; Wiley: New York, 1976; Chapter 7.

[4] Morgehenn, R.; Merz, L.; Haase, W. *J. Chem. Soc., Dalton Trans.* **1980**, 1703.

[5] Marsh, W. E.; Patel, K. C.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1983**, *22*, 511.

[6] Hatfield, W. E. *Comments Inorg. Chem.* **1981**, *1*, 105.

[7] Hatfield, W. E. *Inorg. Chem.* **1983**, 22, 833.

[8] McGregor, K. T.; Losee, D. B.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1974**, *13*, 756.

[9] Hodgson, D. J.; Hale, P. K.; Hatfield, W. E. *Inorg. Chem.* **1971**, *10*, 1061.

[10] Hoffmann, S. K.; Hatfield, W. E. *J. Magn. Reson.* **1983**, *53*, 341.

[11] McGregor, K. T.; Hatfield, W. E. *J. Chem. Phys.* **1976**, *65*, 4155.

[12] McGregor, K. T.; Hatfield, W. E. *J. Chem. Phys.* **1975**, *62*, 2911.

0020-1669/85/1324-1194$01.50/0