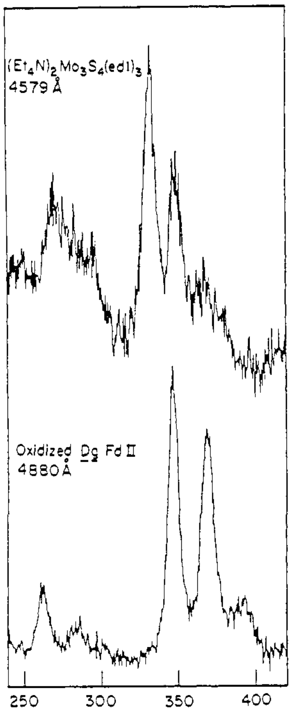

Figure 2. Resonance Raman spectra[22] of $[(C_2H_5)_4N]_2[Mo_3S_4(SCH_2CH_2S)_3]$ (solid state, 10-cm^{-1} spectral slit width) and Dg Fd II (frozen solution, 6-cm^{-1} spectral slit width) obtained via backscattering by using 4579- and 4880-Å Ar^+ Laser excitations, respectively (at liquid N_2 temperature). Observed frequencies: (a) $[N(C_2H_5)_4]_2[Mo_3S_4(SCH_2CH_2S)_3]$, 382, 356, 334, 287, and 270 cm^{-1}; (b) Dg Fd II, 392, 368, 347, 285, and 267 cm^{-1}.[21]

formulation for the Fe–S core.[20,21] These Fe_3S_4 centers have a distinct resonance Raman signature.[21] Although the metal atoms in the present structure are not iron atoms, the Mo_3S_4 core in the present communication is stoichiometrically and possibly structurally analogous to Fe_3S_4 cores in these proteins. The resonance Raman spectrum of $Mo_3S_4(SCH_2CH_2S)_3{}^{2-}$ and that of the 3Fe ferredoxin (Fd) from *Desulfovibrio gigas* (Dg), Fd II,[21] are shown in Figure 2. The resemblance between the spectra is striking with the shift being in the direction and of the magnitude expected for substitution of Fe by Mo. Detailed vibrational analyses of this and other inorganic model compounds are under way to provide information relevant to the analysis of the data in the protein systems.

Acknowledgment. We thank Prof. T. G. Spiro for his encouragement of the resonance Raman studies, carried out in his laboratories with support from NIH Grant GH13498-NIH. We also thank Dr. C. S. Day of Crystalytics Co. for carrying out the single-crystal diffraction study.

Registry No. 1, 88765-89-3; **2**, 88765-91-7; $(NH_4)_2[Mo_3S(S_2)_6]$, 67031-31-6; $Mo_3S_{13}{}^{2-}$, 88765-92-8; S, 7704-34-9; $^-SCH_2CH_2S^-$, 52724-23-9; PPh_3, 603-35-0; CN^-, 57-12-5; dibenzyl trisulfide, 6493-73-8.

Supplementary Material Available: Crystallography details, including tables of atomic coordinates, thermal parameters bond lengths and bond angles, structure factors, and perspective drawings of TEA^+ cations (38 pages). Ordering information is given on any current masthead page.

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Configuration Chirality of Metal–Metal Multiple Bonds: Preparation and Circular Dichroism Spectrum of Tetrachlorobis-[(*S*,*S*)-2,3-(diphenylphosphino)butane]dimolybdenum (Mo_2Cl_4(*S*,*S*-dppb)$_2$)

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Chiral compounds containing a metal–metal multiple bond present an exciting new area of study. Complexes have been reported in which an $Mo\overset{4}{-}Mo$ unit is bridged by (*S*)-leucinate,[1] (*S*)-isoleucinate,[2] or (*R*)-mandelate[3] ions. In all cases the bridging groups are planar, the ligating atoms are practically eclipsed,[3] and the chirality is due effectively to the asymmetric carbon atoms. which are at some distance from the Mo_2O_8 core. Preliminary circular dichroism (CD) spectra have been recorded for the mandelate complex, and as expected the optical activity is rather weak as the dimolybdenum chromophore is not intrinsically chiral. Qualitative CD spectra have been published[4] for solutions of $Mo_2(CH_3COO)_4$ in which one or more of the acetate groups have been replaced by chiral carboxylate ions. The structures of the species present are not known but again the chirality can arise only from the vicinal effect of an asymmetric carbon atom at some distance from the chromophore.

We reasoned that the most informative complexes to investigate would be ones that are configurationally chiral[5] due to two sets of MX_4 or MX_2Y_2 units being twisted with respect to each other about the metal–metal bond. For such complexes it is possible to derive a direct relationship between the absolute configuration and the CD of the $\delta \rightarrow \delta^*$ transition. We accordingly present the first report of the preparation and CD spectrum of a configurationally chiral metal–metal bonded complex, Mo_2Cl_4(*S*,*S*-dppb)$_2$, where *S*,*S*-dppb represents the $Ph_2PCH(CH_3)CH(CH_3)PPh_2$ ligand, (*S*,*S*)-2,3-(diphenylphosphino)butane.

Mo_2Cl_4(*S*,*S*-dppb)$_2$ has been prepared in two different ways: (1) by refluxing $K_4Mo_2Cl_8$ with 2 equiv of *S*,*S*-dppb in methanol for 2 h, (2) by reaction of $Mo_2(O_2CCF_3)_4$ with Me_3SiCl and *S*,*S*-dppb in THF. The green solid is soluble in a variety of organic solvents including THF, MeOH, EtOH, CH_3CN, CH_2Cl_2, and benzene, and solutions appear to be stable for periods of weeks. The compound gave a satisfactory elementary analysis. Its identity was conclusively confirmed and the molecular structure revealed by two independent x-ray crystal structure determinations.[6]

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[1] Bino, A.; Cotton, F. A. Fanwick, P. E. *Inorg. Chem.* **1980**, *19*, 1215.

[2] Bino, A.; Cotton, F. A. *Inorg. Chem.* **1979**, *18*, 1381.

[3] Cotton, F. A.; Falvello, L. R.; Murillo, C. A. *Inorg. Chem.* **1983**, *22*, 382. The mean twist angle about the Mo–Mo bond (not stated in the paper) is +1.4°.

[4] Snatzke, G.; Wagner, U.; Wolff, H. P. *Tetrahedron* **1981**, *37*, 349.

[5] This sort of system is clearly of the type that is said to contain an *inherently dissymmetric* chromophore, whereas those mentioned above are likely to be examples of a *symmetric chromophore in a chiral molecular environment*. Somewhat different theroretical approaches have been developed for these two classes. See, for example, Mason (Mason, S. F. "Molecular Optical Activity and the Chiral Discriminations", Cambridge University Press: New York, 1982), for details and literature references.

[6] Compound **1** (Mo_2Cl_4(*S*,*S*-dppb)$_2$·THF) forms crystals in space group $P2_12_12_1$ with a = 14.57 (1) Å, b = 36.69 (1) Å, c = 11.84 (1) Å. Compound **2** (Mo_2Cl_4(*S*,*S*-dppb)$_2$·4CH_3CN) also crystallizes in space group $P2_12_12_1$ with a = 13.535 Å, b = 21.044 Å, c = 23.214 Å, and Z = 4 in each case. The dimensions of the Mo_2Cl_4(*S*,*S*-dppb)$_2$ molecule in the two cases were virtually identical: D(Mo–Mo) = 2.150 (3) Å and 2.143 (2) Å for **1** and **2**, respectively, while the P–Mo–Mo–P torsion angles were −24.3°, −25.2° in **1** and −23.2°, −22.6° in **2**. The structure of **2** was obtained in collaboration with K. W. Muir and Lj. Manojlovic-Muir.

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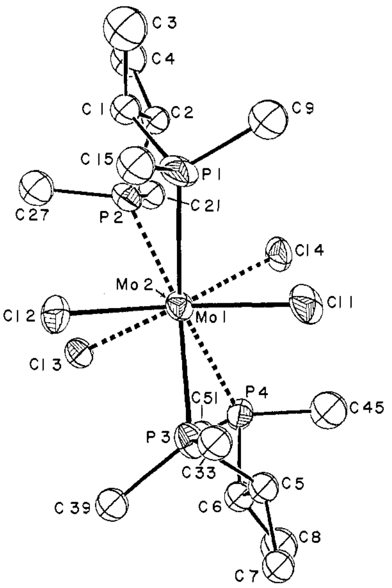

Figure 1. View of the Mo_2Cl_4(S,S-dppb)$_2$ molecule down the Mo(1)–Mo(2) axis, showing the negative helicity.

Figure 1 shows a view down the Mo(1)–Mo(2) axis. The absolute configuration is seen to be that of a left-handed (Λ) helix, with a mean twist angle of ca. 23°.

The Mo_2Cl_4(S,S-dppb)$_2$ molecule invites comparison with others[7] of similar composition, viz., M_2X_4(diphos)$_2$, where M may be Re, W, or Mo, X may be Cl or Br, and diphos represents any 1,2-diphosphinoethane ligand such as $Me_2PCH_2CH_2PMe_2$(dmpe), $Ph_2PCH_2CH_2PPh_2$(dppe), or, by extension, $Ph_2PCH_2CH_2AsPh_2$ (arphos). In all other cases, there has been evidence for the formation of two isomers, one (α) with chelating diphos ligands and one (β) with bridging ligands. In the case of W_2Cl_4(dppe)$_2$, the structures of both isomers have been determined.[8] By neither of our preparative methods have we obtained a proven sample of α-Mo_2Cl_4(S,S-dppb)$_2$ although it is not impossible that it might be among the additional products of preparative method 2. For Mo_2Cl_4(dppe)$_2$ it has been found that the α isomer spontaneously converts to the β form with a half-life of ca. 15 h at room temperature. We have also prepared both isomers of Mo_2Cl_4(R-dppp)$_2$, where R-dppp is (R)-$Ph_2PCH(CH_3)CH_2PPh_2$; the half-life for isomerization from the α to β form is approximately 15 min. It seems, therefore, that for all three diphosphines, dppe, R-dppp, and S,S-dppb, the bridged isomer is thermodynamically more stable, such stability being markedly increased with successive methylation of the ligand backbone.

The fact that while the α and β forms of Mo_2Cl_4(dppe)$_2$ are green and brown, respectively, the β-Mo_2Cl_4(S,S-dppb)$_2$ is green may seem, superficially, to be inconsistent, but it is an understandable consequence of the strengths and positions of the absorption bands between 600 and 850 nm, as shown in figure 2. This will be discussed fully in future publications.

The CD spectrum of Mo_2Cl_4(S,S-dppb)$_2$ (figure 2) shows strong Cotton effects under both the $\delta \rightarrow \delta^*$ transition (at 13 700 cm^{-1}) and the next highest energy absorption (at 21 050 cm^{-1}). The latter transition has a dissymmetry factor g ($=\Delta\epsilon/\epsilon$) of 8×10^{-2}. A g factor of this magnitude usually indicates that the transition is magnetic-dipole allowed in the parent achiral chromophoric symmetry[9] and provides strong evidence that the 21 050-cm^{-1} transition of Mo_2Cl_4(S,S)-dppb)$_2$ correlates with the magnetic-dipole allowed ${}^1A_{1g} \rightarrow {}^1E_g$ transition, which has been calculated

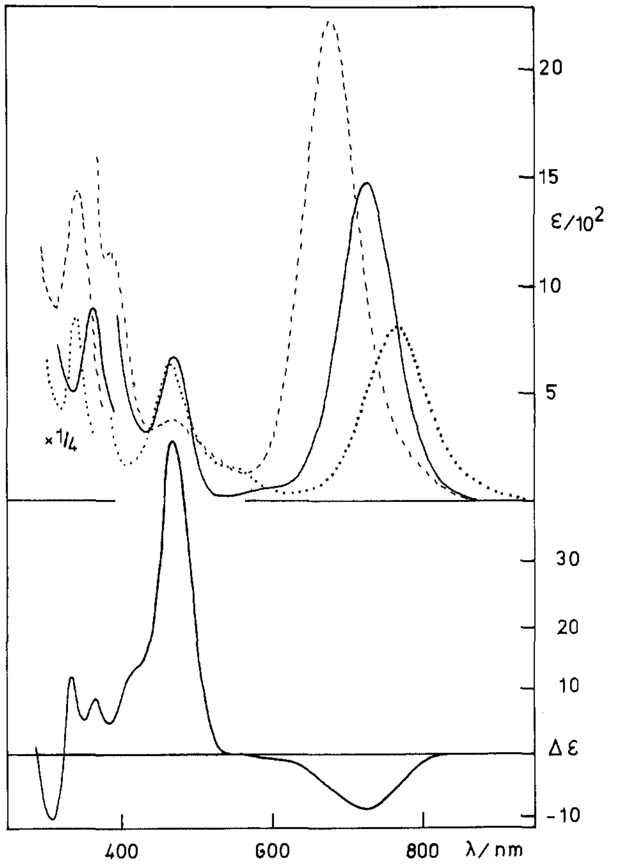

Figure 2. Absorption and CD spectra of Mo_2Cl_4(S,S-dppb)$_2$ (solid curves) and the absorption spectra of the α (chelated) and β (bridged) isomers of Mo_2Cl_4(dppe)$_2$ (dashed and dotted curves, respectively). All spectra are in CH_2Cl_2 solution.

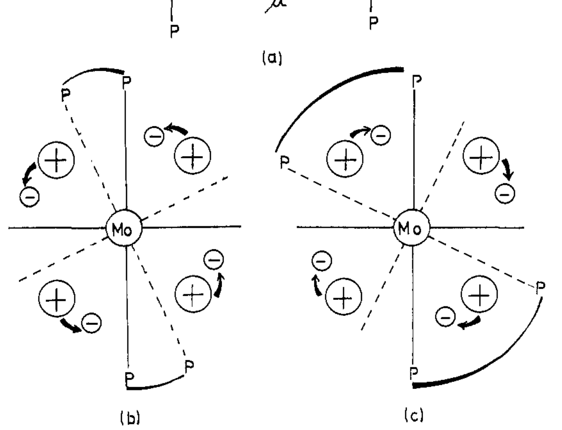

Figure 3. Transient charge distributions for the $\delta \rightarrow \delta^*$ transition of the $Mo_2X_4Y_4$ chromophore: (a) in the fully eclipsed geometry the transition is electric-dipole allowed in a direction along the Mo–Mo bond; (b) on rotating the rear set of ligators through an angle of less that 45° in the counterclockwise direction, the transitional charge distribution is that of a left-handed helix; (b) on rotating counterclockwise through an angle of greater than 45°, the transition gives rise to a right-handed helical charge displacement.

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[7] See a forthcoming paper by P. A. Agaskar and F. A. Cotton, in which the structure of β-Mo_2Cl_4(dppe)$_2$ is reported, for a review of available structural data on such molecules.

[8] Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1981**, *20*, 3880.

[9] A good rule of thumb is that $g > 10^{-2}$ indicates a magnetic-dipole allowed, electric-dipole forbidden transition in the achiral parent symmetry, and vice versa for $g < 10^{-2}$: Mason, S. F. "Optical Activity and the Chiral Discriminations": Cambridge University Press: New York, 1983.

to occur at around 23 000 cm^{-1} in the $[Mo_2Cl_8]^{4-}$ ion.[10]

If the absorption at 13 700 cm^{-1} is assumed to be due to the pure metal-localized $\delta \rightarrow \delta^*$ excitation, then the sign of the associated Cotton effect may be related to the absolute configuration of the complex in the following way. In the fully eclipsed configuration the transition is electric-dipole allowed in a direction along the Mo–Mo bond (figure 3a). Twisting the rear MoP_2Cl_2 group (viewed along the Mo–Mo bond) counterclockwise through an angle of between 0° and 45° results in the $Mo_2P_4Cl_4$ unit taking a left-handed helical configuration (Figure 3b). In this absolute configuration the $\delta \rightarrow \delta^*$ transition gives rise to a left-handed helical charge displacement and so to a negative Cotton effect. In the fully staggered configuration there is no overlap between the d_{xy} orbitals on the two Mo atoms and the absorption and CD spectra have zero intensity for a pure $\delta \rightarrow \delta^*$ transition. When the twist angle is between 45° and 90° the $Mo_2P_4Cl_4$ unit takes a right-handed helical configuration (Figure 3c) and the CD of the $\delta \rightarrow \delta^*$ transition should be positive. Rotation of the rear MoP_2Cl_2 group in the clockwise direction produces the opposite absolute configurations and Cotton effects.[11]

In summary, we have shown that the optical activity of the $\delta \rightarrow \delta^*$ transition can be explained by a simple metal-localized model and have established CD as a useful method of predicting the absolute configuration of configurationally chiral dimolybdenum compounds.

Acknowledgment. We thank the U. S. National Science Foundation for financial support, the U. K. S.E.R.C. for a studentship (to I.F.F.), and L. McGhee for technical assistance.

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[10] Norman, I. G., Jr.; Kolari, H. J. *J. Am. Chem. Soc.* **1979**, *101*, 1752.

[11] Note that the absolute configuration *as defined by the helicity of the bridging phosphines* is Λ for a counterclockwise rotation irrespective of whether the twist angle is greater or less than 45°. The CD, however, is governed by the *helicity of the chromophore*, which does change with the magnitude of the torsion angle. A similar situation is found in tris-chelated diamine complexes: Λ-$[Co(en)_3]^{3+}$ and Λ-$[Co(tn)_3]^{3+}$ have d–d circular dichroism of opposite sign, despite having the same absolute configuration as defined by their chelate rings, because their ligating atoms have opposite signed trigonal twists. See, for example: Peacock, R. D.; Stuart, B. *Coord. Chem. Rev.* **1982**, *46*, 129.

Uranium–Carbon Multiple-Bond Chemistry. 3. Insertion of Acetonitrile and the Formation of a Uranium–Nitrogen Multiple Bond[1]

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Metal–carbon multiply bonded alkylidene, M═CR$_2$, and alkylidyne, M≡CR, complexes are isoelectronic to imido, M═NR, and nitrido complexes, M≡N, respectively.[2,3] The possibility of similar reactions at metal–carbon multiple bonds and at their metal–nitrogen counterparts has been raised in several recent studies.[4,5] While there are no reported imido actinide complexes, we have recently characterized compounds that contain uranium–carbon multiple bonds[6-8] and have uncovered an extensive chemistry for these species.[1,9] It thus seemed reasonable that uranium–nitrogen multiply bonded species might also be isolated.

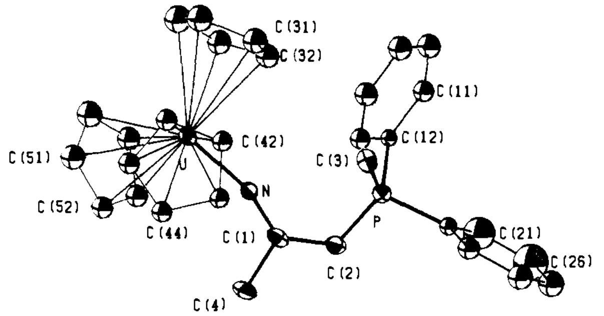

Figure 1. ORTEP representation of the $Cp_3UNC(Me)CHP(Ph)_2Me$ molecule.

Table I. Bond Lengths (Å) and Bond Angles (deg) with Their Standard Deviations for $Cp_3UNC(Me)CHP(Ph)_2Me$

atoms	distances	atoms	angles
U–N	2.06 (1)	U–N–C(1)	163 (1)
N–C(1)	1.34 (2)	N–C(1)–C(4)	118 (1)
C(1)–C(2)	1.39 (2)	C(2)–C(1)–C(4)	114 (1)
C(2)–P	1.74 (2)	C(1)–C(2)–P	123 (1)
C(3)–P	1.83 (2)		
C(12)–P	1.79 (1)		
C(22)–P	1.78 (1)		
C(1)–C(4)	1.54 (3)		

The synthesis of an (imido)uranium complex results from the reaction of $Cp_3U{=}CHP(Ph)_2Me$ with MeCN in equimolar quantities in toluene at 55 °C for 24 h.

$$\underset{\mathrm{I}}{Cp_3U{=}CHP(Ph)_2Me} + MeCN \rightarrow \underset{\mathrm{II}}{Cp_3UNC(Me)CHP(Ph)_2Me}$$

$$Cp = \eta^5\text{-}C_5H_5,\ Ph = C_6H_5,\ Me = CH_3$$

Evaporation of the volatile components of this mixture leaves a red solid which, after recrystallization, produces a 50% yield of II.[10] The ^1H NMR of this material can be assigned as follows: δ -20.6 (15 H, UCp_3), 4.83 (4 H, $P(Ph)_2$), 1.98 (4 H, $P(Ph)_2$), 3.12 (2 H, $P(Ph)_2$), 35.3 (J_{PCH} = 27 Hz, 1 H, P(CH)), -7.38 (3 H, P(Me)), 47.8 (3 H, $N(CH_3)$)). The IR spectrum exhibits peaks typical of the $CHP(Ph)_2Me$ moiety but does not contain any in the 2270 cm^{-1} region where coordinated nitriles show characteristic frequencies.[11] Since these data are insufficient to allow II to be adequately characterized, an X-ray crystal structure determination was undertaken.

Dark red crystals of $Cp_3UNC(Me)CHP(Ph)_2Me{\cdot}C_6H_5CH_3$ belonging to the triclinic space group $P\bar{1}$ with unit cell parameters a = 12.789 (2) Å, b = 14.479 (5) Å, c = 10.389 (3) Å, α = 94.39 (2)°, β = 110.7 (2)°, γ = 67.68 (2)°, V = 1661.2 (8) Å^3, and Z = 2 were grown from a 1:1 mixture of toluene and heptane. Data collection and reduction were carried out as described previously,[7,12] and the structure was routinely solved using Patterson and Fourier methods. Least-squares refinement using rigid group parameters for the Cp and Ph rings and anisotropic thermal parameters for the nongroup atoms converged at R_1 = 0.067 and R_2 = 0.082 using 5144 unique absorption corrected reflections for which $F_o^2 > 3\sigma(F_o^2)$. Each of the Cp groups is disordered over two positions related by rotation about the vector from the Cp centroid to the uranium atom. Each of the two orientations

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[1] Paper 2 in this series: Cramer, R. E.; Higa, K. T.; Pruskin, S. L.; Gilje, J. W. *J. Am. Chem. Soc.* **1983**, *105*, 6749-6750.

[2] Dehnickle, K.; Strahle, J. J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 413-426.

[3] Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123-175.

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[9] Cramer, R. E.; Maynard, R. B.; Paw, J. C.; Gilje, J. W. *Organometallics* **1982**, *1*, 869-871.

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[11] Fischer, R. D.; Klähne, E.; Kopf, J. *Z. Naturforsch., B* **1978**, *33B*, 1393-1397.

[12] Cramer, R. E.; VanDoorne, W.; Dubois, R. *Inorg. Chem.* **1975**, *14*, 2462-2466.

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