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Synthesis and Characterization of New Adducts of Cobalt Bis(2,4-pentanedionate). Molecular Structure of a Cis Complex: Cobalt Bis(2,4-pentanedionate) *N*,*N*,*N*′,*N*′-Tetraethyl-1,2-diaminoethane

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The synthesis and characterization of several new adducts of cobalt(II) 2,4-pentanedionate are described. In particular, the cis structure of several chelating tertiary diamines is confirmed by X-ray crystallography on the adduct with *N*,*N*,*N*′,*N*′-tetraethyl-1,2-diaminoethane. Crystals of the complex with molecular formula $C_{20}H_{38}CoN_2O_4$ are monoclinic with space group *Cc*, $a = 10.127$ (2), $b = 19.197$ (4), $c = 12.230$ (3) Å, $\beta = 90.39(2)°$, and $Z = 4$. The steric constraints on ligand complexation are also investigated.

Introduction

The reaction between various bases and cobalt(II) acetylacetonates to form adducts has been known at least since 1904.[1] In the 1960s, many of these compounds were characterized by a wide variety of techniques.[2] Both exchange phenomena[3] and spectroscopic results[3,4] have been examined extensively. Their use in catalysis has been, however, slight.[5] We were interested in further exploration of their possible catalytic behavior, since a diversity of β-diketonates and bases might allow a range of activities based on the appropriate steric and electronic properties of the ligands.

In this context, we wish to report the synthesis of a variety of $Co(acac)_2$ adducts and their properties. These complexes include the first preparation of tertiary amine adducts. In particular we have structurally characterized the *N*,*N*,*N*′,*N*′-tetraethyl-1,2-diaminoethane adduct, which is naturally constrained to adopt the cis configuration. This is the first example of a structurally characterized cis adduct of $Co(acac)_2$.

Experimental Section

Apparatus and Materials. While all reactions were carried out under an atmosphere of nitrogen, workup and purification of the products were performed open to air. Infrared spectra were recorded on a Perkin-Elmer 598 spectrometer. Field desorption mass spectrometry was performed on a Finnegan MAT 731 instrument. Analysis was carried out internally by the Materials Characterization & Engineering Support Operation. All compounds were prepared in a similar way.

Sample Synthesis. Cobalt acetylacetonate (1.04 g, 4 mmol) is added to a 50-mL two-neck flask. Freshly distilled toluene (30 mL) and a stir bar are subsequently added. One neck is stoppered, and the other neck is fitted with a distillation head. The flask is then heated, and any residual H_2O bound to $Co(acac)_2$ is azeotropically removed. When the distillation temperature reaches 110 °C, the heat is then removed. The ligand may be added through the other neck when the refluxing has subsided. The ligand is usually added in 10% excess. If the ligand is a solid, it may be added in a portion of toluene. Often there is an immediate color change. Depending on the solubility characteristics of the ligand, the product may be immediately filtered from the reaction flask upon cooling or crystallized from the solution after removal of a portion of the solvent by rotary evaporation. Recrystallization may be effected from hexane/toluene mixtures at −20 °C. Yields are reported in Table I.

X-ray Structural Determination of 8. Dark red crystals were obtained by recrystallization from hexane at −25 °C. The crystals were tabular with dimensions of 0.3 × 0.2 × 0.1 mm. Data were collected at 21 °C with the use of a Nicolet P3F automated single-crystal diffractometer and Mo Kα radiation. Crystal data and refinement results are summarized in Table II. The structure was solved by direct methods using the SHELXTL program package.[6] No absorption corrections were applied. The function used for least-squares minimization was $\sum w(|F_o| - |F_c|)^2$. The original weights are described by $w = [\sigma^2(F) + 0.00139F^2]^{-1}$. Some decomposition of the crystal was noted after the collection was complete.

Results and Discussion

Previous work demonstrated the ability of $Co(acac)_2$ to coordinate with a wide variety of bases. Tolman's research has emphasized that steric factors play a more important role than basicity in ligand dissociation processes.[7] In this context, it was of interest to probe the stability of secondary and tertiary amine adducts. Additional comparisons may be made by contrasting the properties of chelating diamines, constrained to adopt a cis geometry, with those of monodentate amines, which typically yield trans complexes.

While adducts of primary amines[8] and pyridines are numerous, as both monodentate ligands and chelates,[9] there are very few instances of secondary[10] or tertiary amine adducts. The synthetic procedure used to prepare all the complexes was analogous to that of Ellern and Ragsdale.[2] Typically, any residual water in $Co(acac)_2$ was azeotropically removed by distillation with toluene. The ligand was then added to the hot solution. Reaction is usually rapid, often evidenced by an immediate change in the color of the solution. Initial attempts to form amine adducts with simple tertiary amines such as triethylamine or dimethylbenzylamine led only to isolation of starting material. Further experiments with trimethylamine and quinuclidine, both of which form adducts, demonstrated the feasibility of incorporating a relatively unhindered tertiary center. In contrast to the results with triethylamine, the chelating ligand *N*,*N*,*N*′,*N*′-tetraethyl-1,2-diaminoethane readily forms a 1:1 adduct with $Co(acac)_2$. Similarly, *N*,*N*′-di-*tert*-butyl-1,2-diaminoethane reacts readily, while diisopropylamine does not form an isolable adduct. We have also prepared the complex with 1,2-bis(diphenylphosphino)ethane as a ligand.

A summary of the physical properties of the new compounds is compiled in Table I. As the spectroscopic properties of such complexes are well understood, they will not be discussed here. Satisfactory analysis was obtained for most of the compounds

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(1) Biltz, W.; Clinch, J. A. *Z. Anorg. Allg. Chem.* **1904**, *40*, 221.

(2) For reviews, see: Mehrota, R. C.; Bohra, R.; Gaur, D. P. *Metal β-Diketonates and Allied Derivatives*; Academic: New York, 1978. Fackler, J. P., Jr. *Prog. Inorg. Chem.* **1966**, *7*, 361. Graddon, D. P. *Coord. Chem. Rev.* **1969**, *4*, 1. For specific examples, see: Cotton, F. A.; Elder, R. C. *Inorg. Chem.* **1966**, *5*, 423. Fackler, J. P., Jr. *Inorg Chem.* **1963**, *2*, 266. Ellern, J. B.; Ragsdale, R. O. *Inorg. Synth.* **1968**, *11*, 82. Hashagen, J. T.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 2821. Dwyer, F. P.; Sargeson, A. M. *J. Proc. R. Soc. N.S.W.* **1956**, *90*, 29.

(3) Lincoln, S. F. *J. Chem. Soc., Dalton Trans.* **1973**, 1896. Kluiber, R. W.; Thaller, F.; Low, R. A.; Horrocks, W. D., Jr. *Inorg. Chem.* **1970**, *9*, 2592. La Mar, G. N. *J. Am. Chem. Soc.* **1970**, *92*, 1806.

(4) (a) Niven, M. L.; Percy, G. C. *Transition Met. Chem.* (*Weinheim, Ger.*) **1978**, *3*, 267 and references therein. (b) Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1980**, *19*, 3027.

(5) Brunner, H.; Hammer, B. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 312. Sandy, C. A. Belg. Patent 877973, 1980. Suzuki, A.; Mochizuki, A.; Minamide, N.; Shirai, H.; Hojo, N. *Nippon Kagaku Kaishi* **1976**, *4*, 663.

(6) Sheldrick, G. M. "SHELXTL, Program System for X-Ray Structure Determination"; Cambridge University: Cambridge, U. K., 1976.

(7) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(8) (a) Haigh, J. M.; Slabbert, N. P.; Thornton, D. A. *J. Inorg. Nucl. Chem.* **1970**, *32*, 3635. (b) Fine, D. A. *J. Inorg. Nucl. Chem.* **1973**, *35*, 4023.

(9) (a) Sankhla, D. S.; Mathur, R. C.; Misra, S. N. *J. Inorg. Nucl. Chem.* **1980**, *42*, 489. (b) Dey, K.; Sen, S. K.; Bhar, J. K. *J. Indian Chem. Soc.* **1979**, *56*, 833. (c) Aggarwal, R. C.; Narayana, D. S. S.; Sekhar, V. C. *Indian J. Chem.* **1981**, *20A*, 419.

(10) Pellacani, G. C.; Battistuzzi, R.; Marcotrigiano, G. *J. Inorg. Nucl. Chem.* **1973**, *35*, 2243.

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Table I. Selected Physical Properties

compd	color	mol wt[a]	yield,[b] %	IR[c] ν, cm^{-1}
Co(acac)$_2$(1,3-diaminopropane) (**1**)	red-orange	331.28	82.0	3265, 1596, 1509, 412
Co(acac)$_2$(*N*,*N*-dimethyl-1,2-diaminoethane) (**2**)	brick red	345.33	70.0	3299, 1601, 1512, 417
Co(acac)$_2$(2-aminopyridine) (**3**)	green-black	351.30	93.0	3425, 3341, 1580, 1511, 437
Co(acac)$_2$(2-amino-6-methylpyridine) (**4**)	green	365.29	68.4	3414, 3344, 1577, 1513, 432
Co(acac)$_2$(*N*,*N*,*N'*,*N'*-tetramethyl-1,2-diaminoethane) (**5**)	pink-red	373.36	95.0	1583, 1510, 403
Co(acac)$_2$(*N*,*N*,*N'*,*N'*-tetramethyl-1,3-diaminopropane) (**6**)	purple	387.38	78.0	1589, 1511, 405
Co(acac)$_2$(*N*,*N'*-di-*tert*-butyl-1,2-diaminoethane) (**7**)	red-purple	429.48	60.0	3245, 1590, 1508, 404
Co(acac)$_4$(*N*,*N*,*N'*,*N'*-tetraethyl-1,2-diaminoethane) (**8**)	red	429.48	74.0	1591, 1510, 408
Co(acac)$_2$(quinuclidine)$_2$ (**9**)	orange	479.53	78.8	1590, 1512, 415
Co(acac)$_2$(1,2-bis(diphenylphosphino)ethane) (**10**)	light purple	655.58	79.5	1585, 1514

[a] Parent ion peaks observed in FDMS for all except **9**. [b] Isolated yield based on Co(acac)$_2$. [c] KBr pellet.

Table II. Crystallographic Data for Co(C$_5$H$_7$O$_2$)$_2$(*N*,*N*,*N'*,*N'*-tetraethyl-1,2-diaminoethane)

formula $C_{20}H_{38}CoN_2O_4$
a = 10.127 (2) Å
b = 19.197 (4) Å
c = 12.230 (3) Å
β = 90.39 (2)°
V = 2377.6 Å^3
Z = 4

fw 429.47
space group *Cc*
T = 25 °C
λ = 0.71069 Å
ρ_{calcd} = 1.19 g cm^{-3}
μ(Mo Kα) = 7.8 cm^{-1}
R = 0.0519
R_w = 0.0589

Table III. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3)

atom	x	y	z	U_{equiv}[a]
Co	0	6496 (1)	0	42 (1)
O(1)	−321 (5)	6504 (2)	1638 (3)	48 (2)
O(2)	1401 (9)	7255 (5)	277 (6)	50 (3)
O(3)	−1349 (10)	7300 (4)	−252 (7)	57 (3)
O(4)	326 (5)	6511 (2)	−1646 (4)	50 (2)
N(1)	−1468 (6)	5577 (3)	−240 (5)	55 (2)
N(2)	1431 (6)	5639 (2)	162 (4)	38 (2)
C(1)	−163 (16)	7036 (5)	2241 (11)	63 (5)
C(2)	673 (9)	7633 (4)	1969 (7)	68 (3)
C(3)	1321 (8)	7721 (4)	1040 (7)	59 (3)
C(4)	−1266 (8)	7701 (3)	−1025 (5)	50 (2)
C(5)	−447 (8)	7624 (4)	−2001 (5)	55 (3)
C(6)	169 (11)	7046 (6)	−2252 (8)	44 (4)
C(7)	−667 (8)	4981 (4)	−354 (6)	61 (3)
C(8)	555 (7)	5005 (3)	424 (7)	59 (3)
C(9)	−872 (10)	7022 (4)	3336 (6)	72 (3)
C(10)	2133 (11)	8334 (4)	961 (8)	86 (4)
C(11)	−1966 (12)	8413 (4)	−831 (7)	92 (4)
C(12)	843 (11)	6976 (5)	−3356 (7)	85 (4)
C(13)	−2374 (14)	5515 (6)	695 (10)	60 (4)
C(14)	−3174 (8)	6087 (4)	1056 (7)	67 (3)
C(15)	−2352 (7)	5774 (4)	−1132 (5)	47 (2)
C(16)	−3384 (16)	5183 (8)	−1452 (11)	71 (5)
C(17)	2241 (9)	5679 (4)	1252 (7)	64 (3)
C(18)	3211 (16)	5156 (8)	1484 (13)	77 (6)
C(19)	2202 (10)	5484 (6)	−870 (8)	39 (3)
C(20)	3266 (9)	6088 (5)	−1001 (7)	71 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table IV. Bond Lengths (Å)

Co–O(1)	2.031 (11)	Co–O(2)	2.060 (14)
Co–O(3)	2.083 (14)	Co–O(4)	2.042 (11)
Co–N(1)	2.324 (13)	Co–N(2)	2.200 (12)
O(1)–C(1)	1.269 (14)	O(2)–C(3)	1.296 (13)
O(3)–C(4)	1.222 (12)	O(4)–C(6)	1.277 (14)
N(1)–C(7)	1.410 (12)	N(1)–C(13)	1.477 (16)
N(1)–C(15)	1.456 (12)	N(2)–C(8)	1.542 (11)
N(2)–C(17)	1.562 (13)	N(2)–C(19)	1.519 (14)
C(1)–C(2)	1.464 (17)	C(1)–C(9)	1.525 (18)
C(2)–C(3)	1.327 (14)	C(3)–C(10)	1.439 (14)
C(4)–C(5)	1.466 (12)	C(4)–C(11)	1.558 (13)
C(5)–C(6)	1.309 (15)	C(6)–C(12)	1.522 (16)
C(7)–C(8)	1.556 (14)	C(13)–C(14)	1.435 (17)
C(15)–C(16)	1.590 (19)	C(17)–C(18)	1.431 (19)
C(19)–C(20)	1.591 (16)		

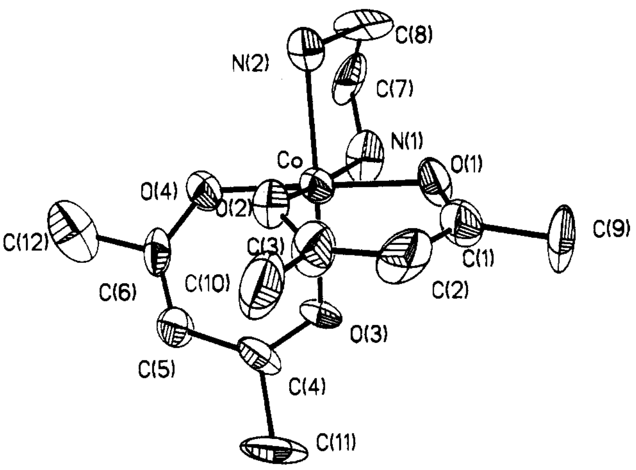

Figure 1. ORTEP plot of Co(C$_5$H$_7$O$_2$)$_2$(TEEDA) (**8**) with the numbering scheme. Hydrogens and the four ethyl groups are omitted for clarity.

Table V. Bond Angles (deg)

O(1)–Co–O(2)	87.0 (4)	O(1)–Co–O(3)	91.8 (4)
O(2)–Co–O(3)	87.2 (5)	O(1)–Co–O(4)	178.8 (3)
O(2)–Co–O(4)	92.1 (4)	O(3)–Co–O(4)	87.4 (4)
O(1)–Co–N(1)	91.4 (3)	O(2)–Co–N(1)	175.4 (4)
O(3)–Co–N(1)	97.2 (4)	O(4)–Co–N(1)	89.6 (3)
O(1)–Co–N(2)	91.5 (3)	O(2)–Co–N(2)	93.5 (4)
O(3)–Co–N(2)	176.7 (4)	O(4)–Co–N(2)	89.3 (3)
N(1)–Co–N(2)	82.2 (4)	Co–O(1)–C(1)	124.0 (7)
Co–O(2)–C(3)	124.1 (7)	Co–O(3)–C(4)	122.2 (8)
Co–O(4)–C(6)	124.3 (6)	Co–N(1)–C(7)	105.1 (5)
Co–N(1)–C(13)	111.3 (6)	C(7)–N(1)–C(13)	111.8 (7)
Co–N(1)–C(15)	106.7 (5)	C(7)–N(1)–C(15)	119.2 (6)
C(13)–N(1)–C(15)	102.7 (8)	Co–N(2)–C(8)	103.3 (5)
Co–N(2)–C(17)	112.5 (7)	C(8)–N(2)–C(17)	99.3 (6)
Co–N(2)–C(19)	114.4 (6)	C(8)–N(2)–C(19)	108.5 (6)
C(17)–N(2)–C(19)	116.7 (7)	O(1)–C(1)–C(2)	124.7 (11)
O(1)–C(1)–C(9)	116.0 (10)	C(2)–C(1)–C(9)	119.3 (9)
C(1)–C(2)–C(3)	125.7 (9)	O(2)–C(3)–C(2)	124.2 (8)
O(2)–C(3)–C(10)	118.5 (8)	C(2)–C(3)–C(10)	116.6 (8)
O(3)–C(4)–C(5)	127.5 (8)	O(3)–C(4)–C(11)	113.6 (8)
C(5)–C(4)–C(11)	118.3 (7)	C(4)–C(5)–C(6)	123.4 (8)
O(4)–C(6)–C(5)	127.0 (9)	O(4)–C(6)–C(12)	112.9 (9)
C(5)–C(6)–C(12)	120.0 (9)	N(1)–C(7)–C(8)	111.9 (6)
N(2)–C(8)–C(7)	110.6 (6)	N(1)–C(13)–C(14)	122.1 (10)
N(1)–C(15)–C(16)	113.5 (8)	N(2)–C(17)–C(18)	119.4 (9)
N(2)–C(19)–C(20)	107.1 (8)		

listed. Since no cis compound had been structurally characterized and many of these compounds crystallize readily, we decided to undertake an X-ray structural study to compare with those of the previously characterized trans adducts.[11]

These include adducts of water, pyridine, and methylquinoline. The average Co–N bond distances in the latter two are 2.187 (5)

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(11) (a) Bullen, G. J. *Acta Crystallogr.* **1959**, *12*, 703. (b) Elder, R. C. *Inorg. Chem.* **1968**, *7*, 1117. (c) Hursthouse, M. B.; Malik, K. M. A.; Davies, J. E.; Harding, J. H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 1355.

and 2.26 (4) Å, respectively. The metal coordination is octahedral with a slight tetragonal distortion. Various dimeric structures of stoichiometry $Co_2(acac)_4L$ and $Co_2(acac)_4L_2$ have also been characterized.[12]

Dark red crystals of Co(2,4-pentanedionate)$_2$(*N,N,N′,N′*-tetraethyl-1,2-diaminoethane) (**8**) were obtained by recrystallization from hexane at −25 °C. Data were obtained at room temperature, and an ORTEP plot of the resulting structure is shown in Figure 1. Selected structural parameters are listed in Tables IV and V.

The compound is a slightly distorted octahedron. There is some asymmetry in the coordination of the amine chelate with Co–N(1) = 2.32 (1) Å and Co–N(2) = 2.20 (1) Å. The former value is quite long, perhaps indicative of steric congestion. As previously determined spectroscopically,[12b] the Co–O bond lengths trans to the nitrogen atoms are slightly longer than those trans to oxygen atoms: 2.06 (1) and 2.08 (1) Å vs 2.03 (1) and 2.04 (1) Å. The latter two values are typical of the Co–O bond lengths in trans complexes.[11] Deviations from planarity for all atoms including the cobalt are less than 0.05 Å for the three planes of the octahedron containing ligands. The largest deviation from a 90° angle is in the amine chelate (∠N(1)–Co–N(2) = 82.2 (4)°).

In conclusion, we have prepared a wide variety of new adducts of $Co(acac)_2$. Preliminary evidence suggests that the thermal dissociation of the ligands varies significantly throughout the series. We hope to utilize such control for catalysis such that the base is released from the metal center upon thermal activation. Our results in this area will appear subsequently.

Acknowledgment. The assistance of Steve Dorn and Nancy Marotta in analytical services is gratefully acknowledged.

Registry No. 1, 116128-88-2; **2**, 116128-89-3; **3**, 116128-90-6; **4**, 116128-91-7; **5**, 73946-62-0; **6**, 116128-92-8; **7**, 116128-93-9; **8**, 116128-94-0; **9**, 116128-95-1; **10**, 116128-96-2; $Co(acac)_2$, 14024-48-7.

Supplementary Material Available: Listings of complete crystallographic details on collection of data (Table SI), anisotropic temperature factors (Table SII), hydrogen coordinates (Table SIII), and elemental analyses of the new compounds (Table SIV) (5 pages). Ordering information is given on any current masthead page.

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(12) (a) Cotton, F. A.; Elder, R. C. *Inorg. Chem.* **1966**, *5*, 423. (b) Hursthouse, M. B.; Laffey, M. A.; Moore, P. T.; New, D. B.; Raithby, P. R.; Thornton, P. *J. Chem. Soc., Dalton Trans.* **1982**, 307. (c) Bertrand, J. A.; Kalyanaran, A. R. *Inorg. Chim. Acta* **1971**, *5*, 167.

Notes

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Synthesis and Characterization of $[Mo_2(S)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4]^{2-}$ and Rational Synthesis of $[M_2(L)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4]^{2-}$ (M = Mo, W; L = O, S) Anions

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Recently the syntheses of $[Mo_2(O)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4]^{2-}$ and $[W_2(S)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4]^{2-}$ have been reported from the oxidation of $[MoO(S_4)_2]^{2-}$ and from the acidification of $[WS_4]^{2-}$ in the presence of manganous chloride, respectively.[1,2] The molybdenum complex has also been synthesized by the nitrosylation of heptamolybdate with hydroxylamine and denitrosylation of [MNO] moiety under basic conditions.[3] The nitrosylation reaction is rather curious because several poly(thiomolybdates) are synthesized by this method where invariably the oxidation state of Mo is quite low.[4] Protonation of $[WS_4]^{2-}$ has long been known to yield several poly(thiotungstate) anions with the involvement of reduction of some tungsten centers.[5–7] Again, it is curious to note that manganous chloride is not involved in the reduction of tungsten center but brings about the oxidation of coordinated sulfido group to disulfido group.[2] When $[Mn(NCS)_4]^{2-}$ is used instead of $MnCl_2$, a mixture of $[W_2(S)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4]^{2-}$ and $[W_2(O)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4]^{2-}$ are isolated.[8] We decided to check the protonation reaction of the thiometalates (Mo, W) in the presence of elemental sulfur, which can serve as an oxidizing agent and contribute to the formation of a disulfido group. With this methodology the synthesis of $[Mo_2(S)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4]^{2-}$ and of the reported compounds, $[Mo_2(O)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4]^{2-}$, $[W_2(S)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4]^{2-}$, and $[W_2(O)_2(\mu\text{-}S)(\eta^2\text{-}S_2)_4]^{2-}$, have been achieved for which the details are presented herein.

Experimental Section

All manipulations were carried out in air unless mentioned otherwise. $(PPh_4)_2MoS_4$, $(AsPh_4)_2MoS_4$, $(AsPh_4)_2MoOS_3$, $(PPh_4)_2WOS_3$, $(AsPh_4)_2WOS_3$, and $(AsPh_4)_2WS_4$ were all made by cation exchange from a solution of the corresponding ammonium salts. $(NH_4)_2MoO_2S_2$ and $(NH_4)_2MoS_4$ were made by literature method.[9] $(Et_2NH_2)_2MoS_4$ was prepared by our method described below. Dimethylamine and diethylamine (AR grade) were used as purchased. Acetonitrile and DMF were distilled and stored over molecular sieves (4 Å) before use.

$[(C_2H_5)_2NH_2]_2MoS_4$.[10] H_2MoO_4 (1.62 g, 0.1 mmol) was dissolved in a mixture of H_2O (10 mL) and Et_2NH (10 mL). H_2S gas was passed into the solution until the red crystals of $(Et_2NH_2)_2MoS_4$ separated out (~30 min). The crystals were washed with cold ethanol and ether and dried under vacuum. Yield: 85%. Anal. Calcd for $C_8H_{24}N_2MoS_4$: C, 25.81; H, 6.45; N, 7.53. Found: C, 25.60; H, 6.38; N, 7.45. IR: 470 ($\nu_{Mo=S}$) cm^{-1}. UV–vis: 467, 316, 241 nm.

$(AsPh_4)_2Mo_2S_{11}$.[11] To a solution of 370 mg (0.37 mmol) of $(Ph_4As)_2MoS_4$ in 10 mL of CH_3CN was added 20 mg (0.62 mmol) of sulfur. After the solution was stirred for 2 min, 0.04 mL of glacial acetic acid in 5 mL of methanol was added into the mixture whereby the orange-red color of the solution changed to dark brown. The solution was stirred for 5 min more, filtered, and cooled in the refrigerator to produce brown crystals. The crystals were filtered, washed with ether, and dried under vacuum. Yield: 25%. Anal. Calcd for $C_{50}H_{43}As_2Mo_2S_{11}N$: C, 44.41; H, 3.18; S, 26.05; N, 1.04. Found: C, 44.10; H, 3.00; S, 26.00; N, 1.01. IR (KBr pellet): 530 (ν_{S-S}), 520 ($\nu_{Mo=S}$) cm^{-1}. UV–vis: 590, 485, 400, 360 nm.

$(AsPh_4)_2W_2O_2S_9$.[11] A 230-mg (0.24-mmol) sample of $[Ph_4As]_2WOS_3$ was dissolved in 7 mL of CH_3CN. Into this clear solution was added 10 mg (0.31 mmol) of sulfur. A green tinge developed, which soon became dark brown. Then 0.1 mL of glacial acetic acid in 5 mL of methanol was added into the mixture whereby the solution became orange-red. After an additional stirring of 1 h, the solution was filtered and cooled (0 °C) to produce orange-red crystals, which were washed with ether and dried in vacuo. Yield: 36%. Anal. Calcd for $C_{50}H_{43}As_2W_2O_2S_9N$: C, 40.13;

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(1) Coucouvanis, D.; Hadjikyriacou, A. *Inorg. Chem.* **1987**, *26*, 1.
(2) Manoli, J. M.; Potvin, C.; Sécheresse, F. *Inorg. Chem.* **1987**, *26*, 340.
(3) Xintao, W.; Shaofeng, L.; Lianyong, Z.; Qiangjin, W.; Jiaxi, L. *Inorg. Chim. Acta* **1987**, *133*, 43.
(4) Müller, A.; Diemann, E. *Adv. Inorg. Chem.* **1987**, *31*, 89.
(5) Sécheresse, F.; Lefebvre, J; Daran, J. C.; Jeannin, Y. *Inorg. Chem.* **1982**, *21*, 1311.
(6) Koniger-Ahlborn, E.; Müller, A. *Angew. Chem.* **1975**, *87*, 598.
(7) Bhaduri, S.; Ibers, J. A. *Inorg. Chem.* **1986**, *25*, 3.
(8) Manoli, J. M; Potvin, C. *Inorg. Chim. Acta* **1987**, *133*, 27.
(9) McDonald, J. W.; Friesen, G. D.; Rosenhein, L. D.; Newton, W. E. *Inorg. Chim. Acta* **1983**, *72*, 205.
(10) $(Me_2NH_2)_2MoS_4$ was synthesized similarly by using dimethylamine in the place of diethylamine.
(11) The corresponding $[Ph_4P]^+$ salts of these complexes can be isolated by using similar methods.

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