acidity range investigated and that our formulation of TiO_2^{3+} may be an oversimplification. It is interesting that all recent ESR studies of superoxotitanium(IV) report a two-lined spectrum.[18,19] While the assignment of these peaks has caused considerable controversy, the concensus is that two distinct species are present in our acidity range. Our results are in agreement with Samuni's careful analysis in which he concludes that the assignment of two different hydrolyzed forms of the superoxo complex may be correct.[18]

The formation constant for superoxotitanium(IV) is apparently very large.[3,20]

$$\mathrm{Ti(IV)} + HO_2 \rightleftarrows \mathrm{Ti^{IV}HO_2} \quad K_f \qquad (20)$$

Our results are consistent with this equilibrium lying far to the right. Even in the presence of cerium(IV) no evidence for significant oxidation of free HO_2 was obtained, even though the rate constant for the HO_2–Ce(IV) reaction is very large.[21] Most previous studies of superoxotitanium(IV) have used solutions containing high concentrations of hydrogen peroxide. It is quite possible that the superoxotitanium(IV) formed in these studies also contained coordinate peroxide. The decay constants reported under these conditions are considerably larger than those we have determined.[3,22] The chemistry associated with the decay process has not been recognized previously.

A potential application of our results is the generation of superoxo complexes in a rather clean environment. The rapid oxidation of a slight excess of TiO_2^{2+} by Ce(IV) produces the superoxotitanium(IV) contaminated only by the excess TiO^{2+} and small concentrations of Ce(III). The possible extension of this procedure to other peroxo complex precursors must await further experimentation. In some cases strong one-equivalent oxidants other than cerium(IV) may be more appropriate.

An internal redox process is an important if not exclusive mode of decay for the superoxo complexes of copper(II), titanium(IV), and vanadium(V). On the basis of the limited data available, these complexes are rather resistant to reaction with external oxidants either by direct reaction or through dissociation of superoxide as free HO_2 in acidic solution. The reactivity of superoxo complexes toward external reductants is unknown, except for our proposal of a rapid reduction of superoxotitanium(IV) by titanium(III).

Registry No. Cl_2, 7782-50-5; Ce, 7440-45-1.

---

(18) Samuni, A. *J. Phys. Chem.* **1972**, *76*, 2207.
(19) Irvine, M. J.; Wilson, I. R. *Aust. J. Chem.* **1979**, *32*, 2283.
(20) Meisel, D.; Czapski, G.; Samuni, A. *J. Am. Chem. Soc.* **1973**, *95*, 4148.
(21) Samuni, A.; Czapski, G. *Isr. J. Chem.* **1970**, *8*, 551.
(22) Irvine, M. J.; Wilson, I. R. *Aust. J. Chem.* **1979**, *32*, 2131.

Contribution from the Department of Chemistry,
University of Florida, Gainesville, Florida 32611

Action of Strong Acids on $M_2(O_2CR)_4$ Species

JOSHUA TELSER and RUSSELL S. DRAGO*

Received April 26, 1983

Treatment of acetonitrile solutions of $Rh_2(O_2CCH_2CH_2CH_3)_4$ and $Mo_2(O_2CCH_3)_4$ with stoichiometric amounts of the strong noncomplexing acids CF_3SO_3H and $HBF_4{\cdot}Et_2O$ gives $Rh_2(O_2CCH_2CH_2CH_3)_2^{2+}$ and $Mo_2(O_2CCH_3)_2^{2+}$, respectively. The rhodium complex is characterized in solution by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. Two derivatives of $Mo_2(O_2CCH_3)_2^{2+}$ were isolated, $[Mo_2(O_2CCH_3)_2(CH_3CN)_4](CF_3SO_3)_2$ (**1**) and $[Mo_2(O_2CCH_3)_2(CH_3CN)_5](BF_3OH)$ (**2**), and characterized by IR and UV–vis spectroscopy.

Introduction

The metal carboxylate dimers $M_2(O_2CR)_4$, where M = Cr, Mo, Ru, Re, Rh, and Cu, have been extensively studied.[1-8] These systems are of interest for several reasons. The presence of two metals in close proximity leads to the possibility of metal synergism; that is, one metal can influence the chemistry at the other metal site, leading to different reactivity than would be expected for monomeric metal systems.[2] Synergism from metal clusters is proposed in a number of biological systems such as the ferredoxins, nitrogenase,[3] cytochrome oxidase, and copper type 3 proteins.[4] Synergism in metal clusters has also been proposed to model metal-surface reactions.[5] Metal carboxylate dimers are ideal systems for studying synergism, for with variation of the metals and their oxidation states there can be wide variation in the metal–metal interaction. Metal–metal bond orders range from 4 in the Mo_2 system to 0 in the Cu_2 system where the Cu atoms are indirectly antiferromagnetically coupled.

In earlier studies from this laboratory,[2] the influence of a synergistic metal–metal interaction on the coordination of ligands to the termini of the metal–metal bond axis was investigated. The metal–metal interaction was found to lead to very effective metal-to-ligand π-back-bonding. Variation in the bridging carboxylate was also shown to have an effect on the metal–terminal ligand bond strength. Our interest in extending this research involves probing the synergistic mechanisms that are possible by having "edge" instead of terminal coordination positions available.

Ligand coordination to these edge (equatorial) positions has been reported for molybdenum(II) carboxylates. The carboxylate becomes monodentate in the process.[7,8] Species such as $Mo_2^{4+}(aq)$[9] and $Rh_2^{4+}(aq)$[10] have been reported, indicating

---

(1) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley-Interscience: New York, 1982; and references therein. Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225.
(2) (a) Richman, R. M.; Kuechler, T. C.; Tanner, S. P.; Drago, R. S. *J. Am. Chem. Soc.* **1977**, *99*, 1055. (b) Drago, R. S.; Tanner, S. P.; Richman, R. M.; Long, J. R. *Ibid.* **1979**, *101*, 2897. (c) Drago, R. S.; Long, J. R.; Cosmano, R. *Inorg. Chem.* **1981**, *20*, 2920. (d) Drago, R. S.; Long, J. R.; Cosmano, R. *Ibid.* **1982**, *21*, 2196. (e) Drago, R. S. *Ibid.* **1982**, *21*, 1697.
(3) Eichhorn, G. L. Ed. "Inorganic Biochemistry"; American Elsevier: New York, 1973.
(4) Solomon, E. I.; Dooley, D. M.; Wang, R.-H.; Gray, H. B.; Cerdonio, M.; Mogno, F.; Romani, G. L. *J. Am. Chem. Soc.* **1976**, *98*, 1029.
(5) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91.
(6) Sheldon, R. A.; Kochi, J. K. "Metal-Catalyzed Oxidations of Organic Compounds"; Academic Press: New York, 1981; p 320.
(7) Girolami, G. S.; Mainz, V. V.; Andersen, R. A. *Inorg. Chem.* **1980**, *19*, 805.
(8) Cotton, F. A.; Lay, D. G. *Inorg. Chem.* **1981**, *20*, 935.
(9) Bowen, A. R.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 3287.
(10) Maspero, F.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 7361.

0020-1669/84/1323-1798$01.50/0 © 1984 American Chemical Society

Table I. NMR Data for the $Rh_2(butyr)_4$ System[a]

	$^{13}C\{^1H\}$[b]				^1H[c]		
	C_1	C_2	C_3	C_4	H_α	H_β	H_γ
$Rh_2(butyr)_4$, CD_3CN soln	194.5	39.6	19.7	13.7	1.97 m	1.38 hex	0.69 t
"exposed-edge" soln							
$Rh_2(butyr)_2^{2+}$	196.8	39.4	19.5	13.7[d]	2.28 t	1.46 m	0.83 t
free butyric acid	182.1	36.3	18.6	13.7[d]	2.67 t	1.69 m	1.0 m
butyric acid	178.2	37.0	19.2	13.9	2.4 t	1.7 m	1.0 t

[a] All spectra run at 25 °C. [b] In ppm relative to Me_4Si, calibrated by using nitrile C of CD_3CN (118.20 ppm relative to Me_4Si). [c] In ppm relative to Me_4Si. [d] Only one signal resolved due to small chemical shift difference.

the stability of the metal dimer without the assistance of bridging or anionic ligands.

It was reported a number of years ago by Wilkinson and co-workers[11,12] that treatment of the metal carboxylate dimer with a strong noncomplexing acid causes protonation of the bridging carboxylate, resulting in formation of a binuclear, coordinatively unsaturated cationic species. These protonations, using acids such as CF_3SO_3H, HBF_4, etc., were reported for $Mo_2(O_2CCH_3)_4$, $Ru_2(O_2CCH_3)_4Cl$, and $Rh_2(O_2CCH_3)_4$ but the products were not fully characterized. Finally, a mechanism has been proposed for the catalysis of olefin hydrogenation by rhodium(II) acetate which involves as an intermediate the species $HRh_2(O_2CCH_3)_3$. This contains a coordinated hydride resulting from the addition of dihydrogen to $Rh_2(O_2CCH_3)_4$ with the loss of CH_3CO_2H.[13] However, this species was not isolated or detected but was proposed on the basis of kinetic data.

The objective of this work is to characterize the species formed when bridging acetates are removed from $M_2(O_2CR)_4$ complexes and to generate these species in weak-donor organic solvents which can stabilize the resulting cation and yet be readily displaced. Accomplishing these objectives would lead to exposed-edge metal–metal bonds whose subsequent chemistry could be systematically investigated.

Results and Discussion

Rhodium. The $Rh_2^{4+}(aq)$ species was first reported by Maspero and Taube[10] in 1968 and reportedly is a relatively stable species. This ion was prepared by reduction of $RhCl^{2+}(aq)$ with $Cr^{2+}(aq)$ and can be converted to $Rh_2(O_2CCH_3)_4(H_2O)_2$ by addition of sodium acetate. This conversion from the cationic dimer to the carboxylate does not appear to be completely reversible. Wilkinson and co-workers[12] claimed to have generated $Rh_2^{4+}(aq)$ from the treatment of $Rh_2(O_2CCH_3)_4$ with strong acids. This claim was subsequently refuted by Wilson and Taube,[14] who proposed that the treatment of $Rh_2(O_2CCH_3)_4$ with hot 1 M aqueous CF_3SO_3H generated $Rh_2(O_2CCH_3)_3^{3+}(aq)$ and $Rh_2(O_2CCH_3)_2^{2+}(aq)$ and no $Rh_2^{4+}(aq)$. The formulation of these species is based on UV–vis spectroscopy and column chromatography. Neither group reported the isolation of any stable rhodium dimer containing zero, two, or three bridging acetates. We found that in acetonitrile such species could be generated by using stoichiometric amounts of acid, but we were not able to isolate a cationic rhodium dimer complex.

Treatment of the purple solution of $Rh_2(butyr)_4$ (butyr = *n*-butyrate) in CH_3CN with 4 equiv of CF_3SO_3H resulted in an immediate color change to dark red. The butyrate ligand was chosen for increased solubility; similar results were obtained with acetate. Trifluoromethanesulfonic acid was chosen since it is a very strong, poorly complexing acid that is somewhat soluble in organic solvents. This red solution in CD_3CN as solvent was examined by using $^{13}C\{H\}$ and ^1H NMR spectroscopy. Upon addition of only 1 or 2 equiv of acid, no color change and no change in the ^{13}C NMR spectrum were observed. However, with 4 equiv of CF_3SO_3H, the red color appears and peaks corresponding to free as well as coordinated butyric acid were observed in the ^{13}C NMR spectrum. The ^1H NMR spectrum also showed free butyric acid. (See Table I.) On the basis of the peak intensities, the dominant species in solution have an average composition of $Rh_2(butyr)_2^{2+}$. The area ratio of peaks corresponding to free and coordinated butyrate was 1:1 in several separately prepared solutions. The ratio of peak areas for the protons H_α:H_β:H_γ for both the free and coordinated butyrate was 2:2:3, as expected. This solution gave no EPR signal at 77 K, indicating that a Rh(II) monomer was not present. This does not prove that the dimer remains intact since disproportionation to EPR-inactive Rh(III) and Rh(I) may have occurred. However, the NMR data suggest that the solution consists of a dimer since the signals for coordinated butyrate, particularly C_1, occur near those for $Rh_2(butyr)_4$, and the color is in contrast to the characteristic yellow or orange color of Rh(I) or Rh(III) complexes. These findings are consistent with our formulation of the dominant solution species as one that contains a metal–metal bond with average composition of $Rh_2(butyr)_2^{2+}$. Attempts to isolate a $Rh_2(butyr)_2^{2+}$ salt were unsuccessful. Evaporation of the "exposed-edge" solution leaves a dark, red, water-soluble oil. Previous workers report that evaporation of the solution from the aqueous titration of $Rh_2(O_2CCH_3)_4$ by CF_3SO_3H led to a deliquescent green oil which was similarly intractable.[12,14] Attempts to isolate a product using BPh_4^- and PF_6^- as counterions were unsuccessful. Some solids were isolated but could not be well characterized.

Another approach that was taken to isolate a $Rh_2(butyr)_2^{2+}$ species involved using a bridging dianionic ligand, Y^{2-}, to form a neutral compound $Rh_2(butyr)_2Y$. This type of compound has precedent in the A-frame series of complexes, which have been found to coordinate a wide variety of molecules to their exposed side.[15-18] The sulfide ligand was chosen since it is used in the A-frame complexes,[18] is readily available, has a high affinity for transition metals, and bridges easily. Anhydrous sulfide was generated directly by addition of Super-Hydride ($LiBHEt_3$, Aldrich) to elemental sulfur, and this solution was added to the red solution of $Rh_2(butyr)_2^{2+}$. A black precipitate immediately formed. The precipitate was insoluble in all solvents tried; thus, it could only be characterized by elemental analysis. (A similarly intractable compound was prepared by using selenide.) The elemental analysis indicated a complex with one or two sulfurs and two butyrate groups. (See Experimental Section.) No molecular ion peaks were detected at *m/e* 412 for $Rh_2(O_2CCH_2CH_2CH_3)_2S$ or *m/e* 446 for $Rh_2(O_2CCH_2CH_2CH_3)_2(SH)_2$. Intense peaks corresponding to H_2S and HS fragments were observed. The compound is possibly a sulfide- or hydrosulfide-bridged rho-

---

(11) Legzdins, P.; Rempel, G. L.; Wilkinson, G. *J. Chem. Soc. D* **1969**, 825.
(12) Legzdins, P.; Mitchell, R. W.; Rempel G. L.; Ruddick, J. D.; Wilkinson, G. *J. Chem. Soc. A* **1970**, 3322.
(13) Hui, B. C.; Teo, W. K.; Rempel, G. L. *Inorg. Chem.* **1973**, *12*, 757.
(14) Wilson, C. R.; Taube, H. *Inorg. Chem.* **1975**, *14*, 2276.
(15) Kubiak, A. P.; Eisenberg, R. *J. Am. Chem. Soc.* **1980**, *102*, 3237.
(16) Cowie, M.; Southern, T. G. *Inorg. Chem.* **1982**, *21*, 246.
(17) Lee, C. L.; Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 2498.
(18) Kubiak, C. P.; Eisenberg, R. *Inorg. Chem.* **1980**, *19*, 2726.

dium polymer which contains two butyrates per rhodium dimer. The dianion of 1,3-propanedithiol, generated in a similar manner, was used in the hope of obtaining more soluble products, but gave only an oil. Rakowski Dubois and coworkers[19] successfully converted the molybdenum sulfide polymer $[(C_5H_5)MoS_x]_y$ to the soluble binuclear complex $[(C_5H_5)MoS(SH)_2]_2$ by stirring the polymer in $CHCl_3$ for 5–7 days under 1 atm of H_2. This was attempted with our rhodium sulfide complex but no dissolution was observed. The solid was also treated with 1-iodoheptane in the hope of alkylating any bridging SH groups to solubilize the complex. However, no reaction was observed, no soluble product was isolated, and the solid recovered showed no increase in carbon or hydrogen content.

Since the above results indicated that we had prepared our "exposed edge", $Rh_2(butyr)_2^{2+}$ ion with weakly coordinating acetonitrile occupying the remaining coordination sites, we proceeded to investigate the reactivity of this ion. The acetonitrile solution of $Rh_2(butyr)_2^{2+}$ showed no change upon exposure to air, and the ^1H NMR spectrum was unchanged. This same solution was sealed in an NMR tube under 1 atm of H_2. There was no visible change in the solution color, and the ^1H NMR spectrum was unchanged. Thus no indication was given that under mild conditions the metal–metal bond could undergo oxidative addition with H_2 to form a metal hydride. $Rh_2(O_2CCH_3)_4$ itself shows no reactivity toward H_2 (1 atm) at temperatures up to 80 °C.[13] Thus, reactivity with H_2 has not been enhanced by "exposing" the metal–metal bond in solution. Furthermore, this complex shows no visible signs of reaction with 1 or 2 equiv of $CH_3O_2CC{\equiv}CCO_2CH_3$, which might be expected to oxidatively add across the metal–metal bond.

Molybdenum. A large number of derivatives of the $Mo_2(O_2CR)_4$ unit exist.[1] Some maintain the bridging ligand framework;[20] in others the bridging ligands have been partly,[21] or wholly,[22] replaced by chelating[21,22] or monodentate[23,24] ligands. In all these complexes the ligands are anionic (e.g. CH_3^-, Cl^-, RCO_2^-, etc.) or very strongly coordinating (e.g. PMe_3).[24] In aqueous solution, Taube and co-workers[25] have generated species such as $Mo_2^{4+}(aq)$ and $Mo_2(en)_4^{4+}$. Gray and co-workers[26] have utilized $Mo_2^{4+}(aq)$ and related complexes to photochemically generate dihydrogen from aqueous solutions. Thus the Mo(II) dimer has an interesting structural chemistry as well as potential catalytic applications.

In contrast to the work with rhodium described above, we were able to isolate two stable complexes in which the molybdenum–molybdenum bond remained intact. The identities of the two complexes were determined by elemental analysis and IR and UV-vis spectroscopy. (See Experimental Section.) Some of the ligands are neither anionic, bridging, nor chelating. Bowen and Taube,[9,25] with their synthesis of $Mo_2^{4+}(aq)$ demonstrated that the Mo_2^{4+} unit can exist in solution without any assistance from bridging ligands. Here we show that two of the bridging acetates in $Mo_2(O_2CCH_3)_4$ can be replaced by acetonitrile, giving an isolable Mo(II) salt. Although molybdenum acetate is completely insoluble in acetonitrile, addition of 2 equiv of CF_3SO_3H leads to immediate formation of an intensely colored purple solution. Subsequent precipitation and recrystallization from toluene–acetonitrile led to isolation of a purple complex of formula $[Mo_2(O_2CCH_3)_2(CH_3CN)_4](CF_3SO_3)_2$ (**1**). This compound is air sensitive and hygroscopic although it is stable indefinitely under an inert atmosphere. The action of CF_3SO_3H on $Mo_2(O_2CCH_3)_4$ has been reported previously.[27] The reaction of neat CF_3SO_3H or excess acid in ethyl acetate with $Mo_2(O_2CCH_3)_4$ at 100 °C is reported to give $Mo_2(O_3SCF_3)_4$ and $Mo_2(EtO_2CMe)_4(CF_3SO_3)_4$, respectively. However, these compounds were synthesized under conditions more extreme than those used here. A second complex was synthesized in this work by using the strong noncomplexing acid $HBF_4{\cdot}Et_2O$. Addition of 4 equiv of $HBF_4{\cdot}Et_2O$ to an acetonitrile suspension of $Mo_2(O_2CCH_3)_4$ led to formation of an intensely colored magenta solution, followed by isolation of an air-sensitive, hygroscopic, magenta compound best formulated as $[Mo_2(O_2CCH_3)_2(CH_3CN)_5](BF_3OH)_2$ (**2**). The possibility exists that cleavage of the Mo_2^{4+} unit occurred and that monomeric species were isolated. However, in both complexes the oxidation state of Mo was found to be 2+ by using Fe^{3+} as an oxidant as described by Taube.[25] Additionally, cleavage can occur without oxidation-state change. Examples include the photolysis of $[Re_2Cl_8]^{2-}$ in acetonitrile to give $ReCl_3(CH_3CN_3)_3$[28] and the reaction of $Mo_2(O_2CCH_3)_4$ with *t*-BuNC to give $Mo(t\text{-}BuNC)_5(O_2CCH_3)_2$.[29] The conditions required were more strenuous than those used here. Irradiation at 366 nm for 24–48 h was needed for photolysis, and in the second case, *t*-BuNC is a far stronger ligand than acetonitrile. However, since the compounds described here, in contrast to $Mo_2(O_2CCH_3)_4$, are soluble in a variety of organic solvents, they may prove useful in solution photochemical studies.[26]

The most conclusive evidence that the Mo–Mo bond remains intact comes from the UV-vis spectra. Bowen and Taube[25] found for $Mo_2^{4+}(aq)$ and $Mo_2(en)_4^{4+}$ absorption bands at 504 nm (ϵ 337 M^{-1} cm^{-1}) and 478 nm (ϵ 483), respectively, and weaker bands at 370 nm (ϵ 40) and 360 nm (ϵ 36.4). A band at 235 nm (ϵ 966) was also observed for $Mo_2(en)_4^{2+}$. The bands at 500 and at 360–370 nm have been assigned to the Mo–Mo $\delta \rightarrow \delta^*$ transition.[26] We find for **1** and **2** absorption bands in acetonitrile at 535 nm (ϵ 864) and 527 nm (ϵ 890), respectively, and weaker bands at 390 nm (ϵ 117) and 370 nm (ϵ 205). In addition, bands were observed at 255 nm (ϵ 7383) and 260 nm (ϵ 7000) for **1** and **2**, respectively. After brief exposure to air, these solutions slowly decompose with a color change from intense purple or magenta to pale yellow. This decomposition was monitored by UV–vis spectroscopy and is shown in Figure 1. The characteristic Mo dimer absorption bands disappear, indicating most likely the appearance of a variety of monomeric Mo species. Prolonged exposure to air gives a blue-green solution characteristic of high-oxidation-state molybdenum.

The UV–vis absorption spectrum of **1** was also obtained in THF solution, giving qualitatively the same results: bands at 490 nm (ϵ 321), 335 nm (ϵ 461), and 277 nm (ϵ 3066). Dissociation of coordinated CH_3CN probably occurs, changing the absorption wavelengths; the shift to shorter wavelengths may result from the replacement of a weakly interacting π-acceptor, CH_3CN, by a σ-only ligand, THF. Thus **1** in THF shows absorptions closest in wavelength and intensity to those of $Mo_2^{4+}(aq)$ and $Mo_2(en)_4^{4+}$. In addition, the THF solution of **1** is for more air sensitive than **1** in acetonitrile, changing color almost immediately upon air exposure, perhaps indicating

---

(19) Rakowski Dubois, M.; VanDerveer, M. C.; Dubois, D. L.; Haltiwanger, R. C.; Miller, W. K. *J. Am. Chem. Soc.* **1980**, *102*, 7456.

(20) Cotton, F. A.; Ilsley, W. H.; Kaim, W. *Inorg. Chem.* **1981**, *20*, 930.

(21) Collins, D. M.; Cotton, F. A.; Murillo, C. A. *Inorg. Chem.* **1976**, *15*, 1861.

(22) Cotton, F. A.; Kolthammer, B. W. S.; Mott, G. N. *Inorg. Chem.* **1981**, *20*, 3890.

(23) San Filippo, J., Jr.; Sniadoch, H. J. *Inorg. Chem.* **1976**, *15*, 2209.

(24) Girolami, G. S.; Mainz, V. V.; Andersen, R. A.; Vollmer, S. H.; Day, V. W. *J. Am. Chem. Soc.* **1981**, *103*, 3953.

(25) Bowen, A. R.; Taube, H. *Inorg. Chem.* **1974**, *13*, 2245.

(26) Trogler, W. C.; Erwin, D. K.; Geoffroy, G. L.; Gray, H. B. *J. Am. Chem. Soc.* **1978**, *100*, 1160.

(27) Abbott, E. H.; Schoenewolf, F., Jr.; Backstrom, T. *J. Coord. Chem.* **1974**, *3*, 255.

(28) Geoffroy, G. L.; Gray, H. B.; Hammond, G. S. *J. Am. Chem. Soc.* **1974**, *96*, 5565.

(29) Girolami, G. S.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2040.

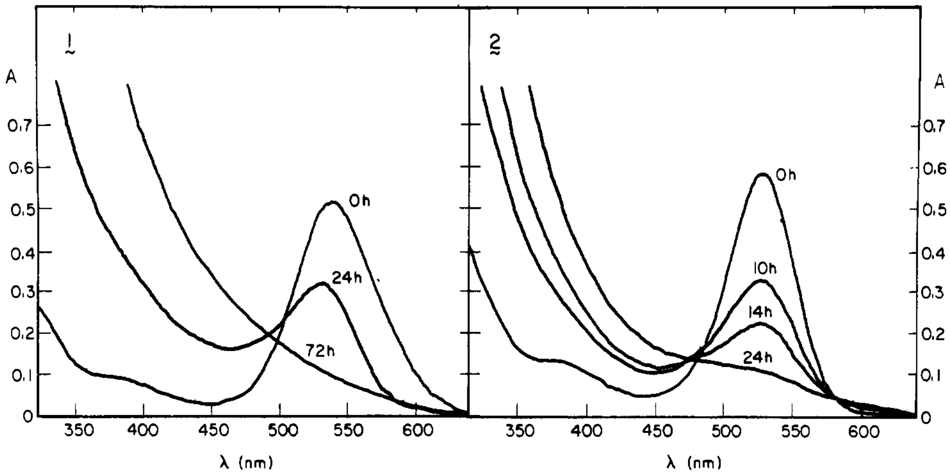

Figure 1. UV–vis spectra of 1 and 2 after exposure to air. [1] = 6.0 × 10^{-4} M in CH_3CN; [2] = 6.5 × 10^{-4} M in CH_3CN.

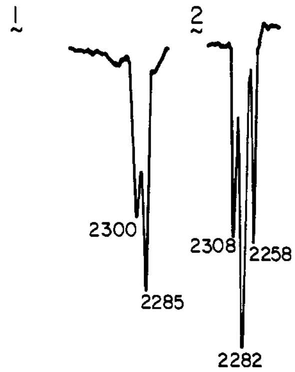

Figure 2. IR spectra (Nujol mull) of 1 and 2 showing ν(CN) (values in cm^{-1}).

poorer stabilization of the Mo_2^{4+} unit.

The IR spectra of 1 and 2 are also of interest and are shown in Figure 2. Very sharp absorption bands corresponding to ν(CN) of the coordinated acetonitriles were observed. In 1 two strong bands were observed at 2300 and 2285 cm^{-1} (Nujol mull). Complex 2 by contrast showed three strong bands at 2308, 2282, and 2258 cm^{-1} (Nujol mull). These shifts to higher frequencies (2266 cm^{-1} for free CH_3CN)[30] are indicative of end-on nitrile coordination with little π-back-bond stabilization.[30] Elemental analysis indicated that there were five acetonitriles in 2. In 1 there are two ν(CN) bands where in 2 a third band results from CH_3CN either in a different coordination environment or from different isomers. Possible geometries for 1 and 2 are shown in Figure 3. In 1 all the CH_3CN's are equivalent while in 2 they are not. Nevertheless, in 1 two bands in the ν(CN) region are observed. This is because in addition to the ν(CN) fundamental a nearby band is often observed which results from a combination of the symmetrical CH_3 deformation and the C–C stretch.[31] Unfortunately, no assignment can be made as to Mo–N stretches. Very few metal organonitrile complex M–N stretches have been conclusively identified, and they are usually weak and widely varying in frequency.[31]

The absorption bands corresponding to the acetate vibrations merit discussion. The IR spectra of metal carboxylate complexes have been extensively studied and proven useful in structural determination.[31a] For 1 no band comparable to $\nu_{asy}(-CO_2)$ was observed (lit.[31a] 1578 cm^{-1}, NaO_2CCH_3).

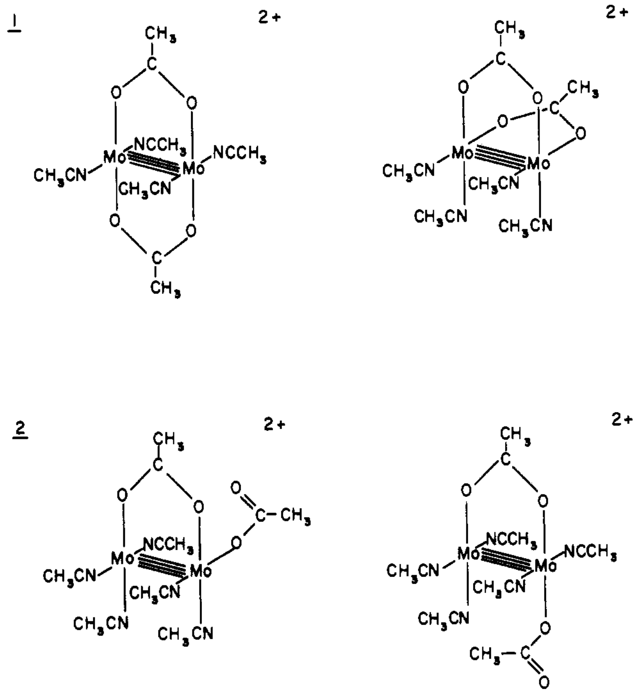

Figure 3. Possible structures for 1 and 2.

However, a band at 685 cm^{-1} was observed which is most likely $\delta(-CO_2)$ (lit.[27] 675 cm^{-1}, $Mo_2(O_2CCH_3)_4$), indicating the presence of bridging acetate. By contrast, complex 2 shows a band at 1647 cm^{-1} which is mostly likely $\nu_{asy}(-CO_2)$ for unidentate rather than bridging acetate. Comparison with known compounds with bridging acetates, such as $Cu_2(O_2CCH_3)_4(H_2O)_2$ ($\nu_{asy}(-CO_2)$ at 1575 cm^{-1}),[31a] and with compounds having monodentate acetate, such as $Ru(O_2CCH_3)_2(CO)_2(PPh_3)_2$ ($\nu_{asy}(-CO_2)$ at 1613 cm^{-1}),[31a] shows that $\nu_{asy}(-CO_2)$ at this high frequency is characteristic of monodentate acetate. Very sharp, intense bands are observed at 680 and 685 cm^{-1}. If one of the acetates is monodentate, this would allow coordination of an additional acetonitrile as shown in Figure 3. The possibility exists that the fifth acetonitrile is axially coordinated. This site in $Mo_2(O_2CCH_3)_4$ is only weakly coordinating, however, since a strong Lewis base such as pyridine only weakly coordinates to this axial position.[1] Finally in 1 a weak band is observable at 410 cm^{-1} which *may* correspond to a Mo–Mo stretch. In the centrosymmetric $Mo_2(O_2CCH_3)_4$ system this vibration is IR inactive; Raman spectroscopy studies[23] on a number of derivatives of the Mo dimer show $\nu(Mo_2)$ occurring from 383 to 404 cm^{-1} with weak to medium intensities. It is possible that noncentrosymmetric

---

(30) Purcell, K. F.; Drago, R. S. *J. Am. Chem. Soc.* **1966**, *88*, 919.

(31) (a) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley-Interscience: New York, 1978; and references therein. (b) Storhoff, B. N.; Lewis, H. C. *Coord. Chem. Rev.* **1977**, *23*, 1.

isomers of **1** are present, allowing observation of $\nu(Mo_2)$ in the IR spectrum. Examples would include $Mo_2(O_2CCH_3)_2[(Pz)_3BH]_2$[21] and $Mo_2(O_2CCH_3)_2(CH_3COCHCOCH_3)_2$,[32] in which the two acetates are cis and there is no center of symmetry; infrared studies were not reported. If an isomer of **1** were present, it would be of C_{2v} symmetry, leading to a symmetry-allowed infrared Mo–Mo stretch. This would most likely be of low intensity due to the small dipole moment change involved. The weak but district band in complex **2** at 405 cm^{-1} may be due to this vibration.

The final area in which IR spectroscopy is of use is in confirming the identity of the counterions. Strong IR absorption bands are observed in **1**, corresponding to noncoordinating $CF_3SO_3^-$. $Mo_2(O_3SCF_3)_4$ shows S–O stretches at 1350, 1110, and 990 cm^{-1}, values comparable to those for compounds with known $CF_3SO_2^-$ coordination.[27] Complex **1** shows bands at 635, 1030, and 1160 cm^{-1} (Nujol mull), values comparable to NaO_3SCF_3 (lit.[33] 630 $\delta(SO_3)$, 1036 $\nu_3(SO_3)$, 1168 $\nu_{as}(SO_3)$ cm^{-1}). Complex **2** shows sharp absorption bands assignable to both B–F and B–OH stretches comparable to those observed in BF_4^- and $B(OH)_4^-$. In a counterion such as BF_3OH^-, all vibrational modes become IR allowed. Weak bands corresponding to the normally IR-forbidden ν_2 and ν_4 modes of BF_4^- at 745 and 378 cm^{-1} (lit.[31] $B(OH)_4^-$, 745 (ν_4), 379 (ν_2) cm^{-1}) in addition to a strong band at 1060 cm^{-1} (lit.[31] BF_4^-, 1060 (ν_3) cm^{-1}) are observed. Finally, two strong bands assigned to $\nu(OH)$ are observed at 3600 and 3530 cm^{-1}. Thus the IR spectrum of **2** supports the formulation of the counterion as $(BF_3OH)^-$, resulting from an impurity in the $HBF_4 \cdot Et_2O$ complex used. Support for this formulation of the counterion is obtained by anion exchange. Complex **2** is dissolved in an acetonitrile solution of excess $(n\text{-}Bu)_4NBF_4$ or $(n\text{-}Bu)_4NPF_6$. Addition of toluene causes precipitation of primarily the BF_4^- or PF_6^- salt. This process can be repeated to effect complete exchange.

^1H NMR spectroscopy was performed on the two complexes, but it did not provide much insight into their structures. Complex **1** showed signals at 4.3 and 2.0 ppm relative to internal Me_4Si in CD_3NO_2. Complex **2** showed signals at 3.0 and 2.1 ppm in CD_3CN. In CD_3CN the upfield signals observed for both **1** and **2** broadened and decreased in intensity over a period of 1 h. This upfield signal corresponds to coordinated CH_3CN and fairly rapid exchange with free CH_3CN. The downfield signal is possibly $CH_3CO_2^-$ although it is rather far downfield for metal-coordinated acetate. Paramagnetic impurities initially present or arising from complex decomposition would cause line broadening and unusual chemical shifts.[34]

A different synthetic approach was used to study the interconvertability of the Mo_2^{4+} derivatives. What is presumably the reported[27] $Mo_2(O_3SCF_3)_4(CF_3SO_3H)$ complex was obtained but not characterized. To this was added acetonitrile, giving an intensely blue solution. Addition of toluene led to formation of a bright blue precipitate. This complex did not give a satisfactory elemental analysis; an IR study indicated coordinated CH_3CN, uncoordinated $CF_3SO_3^-$, and some residual bridging acetate as well as a strong $\nu(OH)$ band. Slow evaporation of the filtrate led to formation of purple crystals whose analysis and IR spectrum corresponded to complex **1**. The initially isolated complex is most likely one in which more than two acetates have been removed, giving a more highly charged species that is less soluble in nonpolar solvents. What is remarkable is that the extreme reaction conditions of the reported synthesis[27] still led to Mo complexes with some bridging acetates as side products while in this work much milder conditions led to quantitative removal of two of the briding acetates. It appears that, as was found with the rhodium systems, the $M_2(O_2CR)_2^{2+}$ unit is quite stable and solvated salts of this species can easily be isolated in good yield whether or not excess acid is used.

Conclusion. This work shows that addition of stoichiometric amounts of strong noncomplexing acids to the metal carboxylate dimer $M_2(O_2CR)_4$, in organic solvents such as acetonitrile results in protonation of the bridging carboxylate and the formation in solution of $M_2(O_2CR)_2^{2+}$. The metal–metal bond remains intact for the rhodium and molybdenum carboxylates. Although ^1H and $^{13}C\{^1H\}$ NMR indicated the presence of $Rh_2(butyr)_2^{2+}$, no molecular solids could be isolated. This parallels the inability to isolate such species in aqueous solution. Nevertheless, the $Rh_2(O_2CR)_2^{2+}$ species generated in this manner is reasonably stable in solution. With molybdenum two stable salts containing the cation $Mo_2(O_2CR)_2^{2+}$ were isolated. Although a variety of complexes containing the Mo_2^{4+} unit have been reported, **1** and **2** are the first in which some of the edge-coordination sites are occupied by neutral, labile organic ligands.

This structure may allow enhanced reactivity of the metal–metal bond, an area of study whose activity has warranted a recent review.[35] Lewis base coordination of axial positions of several metal dimers has been studied;[2] a natural extension of this work would involve probing the reactivity of the edge positions toward Lewis bases. Synergism between the metal atoms has been demonstrated in the axial-coordination studies and may present itself in the edge-coordination studies.

Experimental Section

All operations were carried out under nitrogen by using Schlenk techniques or an inert-atmosphere box. Solvents were distilled before use. Trifluoromethanesulfonic acid was distilled under reduced pressure. Tetrafluoroboric acid–diethyl ether (Pfaltz and Bauer) was used without further purification. Rhodium acetate was synthesized from $RhCl_3 \cdot 3H_2O$ by literature methods.[36] Rhodium butyrate was synthesized from the acetate by exchange with butyric acid.[2] Molybdenum acetate was synthesized from $Mo(CO)_6$ by following the procedure of Martin et al.[37]

$Rh_2(butyr)_2^{2+}$ Solution. $Rh_2(butyr)_4$ (0.328 g, 0.59 mmol) was dissolved in CH_3CN (5.00 mL) to give a purple solution. CF_3SO_3H (0.21 mL, 2.37 mmol) was added. The solution turned dark red immediately. Similar solutions using CD_3CN were used for the NMR work.

Sulfide Complex. To 2 mL of the "exposed-edge" solution (0.092 M based on $Rh_2(butyr)_4$) was added Li_2S (2.5 mL in THF) prepared as follows: THF (1 mL) was added to S (0.0236 g, 0.74 mmol) to make a slurry. Super-Hydride ($LiBH(CH_2CH_3)_3$, 1.5 mL, 1 M in THF, Aldrich) was added dropwise. Gas evolution was vigorous, and a pale yellow solution resulted. Addition of the sulfide solution led to immediate formation of a black precipitate.

Filtration, washing with THF, and overnight drying at 100 °C under vacuum afforded 0.8 g. This compound was insoluble in all solvents attempted and was characterized by mass spectroscopy as previously described and by elemental analysis. Anal. Calcd for $Rh_2(O_2CCH_2CH_2CH_3)_2S$: C, 23.32; H, 3.43; S, 7.78; C:H, 6.80. Found: C, 24.39; H, 3.70; S, 12.53; C:H, 6.81. The high sulfur analysis results from bridging mono- or polysulfide as well as SH units. The selenium compound was prepared in an identical manner but gave an even less satisfactory elemental analysis.

Bis(acetato)tetrakis(acetonitrile)dimolybdenum(II) Bis(trifluoromethanesulfonate) (1). $Mo_2(O_2CCH_3)_4$ (0.40 g, 0.93 mmol) was suspended in acetonitrile (4 mL). It is important that the acetonitrile be degassed by using freeze–pump–thaw cycles with the final vacuum

---

(32) Garner, C. D.; Parkes, S.; Walton, I. B.; Clegg, W. *Inorg. Chim. Acta* **1978**, *31*, 6451.

(33) Miles, M. G.; Doyle, G.; Cooney, R. P.; Tobias, R. S. *Spectrochim. Acta, Part A* **1969**, *25A*, 1515.

(34) Drago, R. S. "Physical Methods in Chemistry"; Saunders: Philadelphia, PA, 1977; Chapter 7.

(35) Chisholm, M. H.; Rothwell, I. P. *Prog. Inorg. Chem.* **1982**, *29*, 1.

(36) Rempel, G. L.; Legzdins, P.; Smith, H.; Wilkinson, G. *Inorg. Synth.* **1971**, *13*, 90.

(37) Martin, D. S.; Newman, R. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2511.

broken by nitrogen; otherwise, decomposition of $Mo_2(O_2CCH_3)_4$ will occur, giving a brown solution. To the suspension was added CF_3SO_3H (0.17 mL, 1.92 mmol). An intensely purple solution formed immediately (use of more than 2 equiv of CF_3SO_3H still leads to isolation of **1** with the possibility of solvent decomposition). Removal of solvent left a dark purple solid, which was dissolved in the minimum amount of acetonitrile (~2 mL), and the mixture was filtered. Addition of toluene (5 mL) to the resulting solution led to formation of a dark purple precipitate after 1 h. Filtration afforded 0.5 g of **1**. Anal. Calcd for $[Mo_2(O_2CCH_3)_2(CH_3CN)_4](CF_3SO_3)_2$: C, 21.77; H, 2.35; N, 7.25; S, 8.30; F, 14.76; Mo, 24.84; O, 20.72. Found: C, 21.83; H, 2.38; N, 7.56; S, 8.28; F, 15.10; Mo, 24.00; O (by difference), 20.85.

Bis(acetato)pentakis(acetonitrile)dimolybdenum(II) Bis(trifluorohydroxyborate) (2). $Mo_2(O_2CCH_3)_4$ (0.71 g, 1.66 mmol) was suspended in acetonitrile as above. To this was added $HBF_4{\cdot}Et_2O$ (0.8 mL, ~6 mmol). An intensely magenta solution formed immediately (excess acid is needed to dissolve most of the $Mo_2(O_2CCH_3)_4$). Removal of solvent left a magenta solid, which was dissolved in acetonitrile (4 mL), and the mixture was filtered. A small amount of yellow needle crystals of unreacted $Mo_2(O_2CCH_3)_4$ remained. Addition of Et_2O (5 mL) to the solution led to rapid formation of a magenta precipitate. Filtration afforded 0.9 g of **2**. The compound was recrystallized from 1:1 toluene–acetonitrile. Anal. Calcd for $[Mo_2(O_2CCH_3)_2(CH_3CN)_5](BF_3OH)_2$: C, 24.55; H, 3.38; N, 10.23; F, 16.65; Mo, 28.02. Found: C, 23.79; H, 3.32; N, 10.02; F, 17.03; Mo, 27.36.

Anion Exchange. $(n\text{-}Bu)_4NBF_4$ (1 g, 3.0 mmol) was dissolved in acetonitrile (5 mL). Complex **2** (0.3 g, 0.44 mmol) was added to the solution. Toluene (5 mL) was then added, leading to formation of a magenta precipitate. This procedure was repeated twice. IR spectroscopy showed a greatly diminished OH stretch and the other bands unchanged. Anal. Calcd for $[Mo_2(O_2CCH_3)_2(CH_3CN)_5](BF_4)_2$: C, 24.41; H, 3.07; N, 10.17; F, 22.06; Mo, 27.86. Found: C, 24.49; H, 3.29; N, 11.77; F, 19.16; Mo, 28.13. Thus, this exchange method is reasonably effective and helps to confirm the anion formulation in **2** as BF_3OH^-.

Molybdenum Trifluoromethanesulfonate Complex. To $Mo_2(O_2CCH_3)_4$ (0.2 g, 0.47 mmol) was added CF_3SO_3H (10 mL). After the mixture was heated at 100 °C with stirring for 1 h, all the solid dissolved. The acid was removed under vacuum, leaving a red solid which presumably corresponds to the $Mo_2(O_3SCF_3)_4(CF_3SO_3H)$ complex described by Abbott et al.[27] Further pumping with heating at 150 °C led to formation of a tan solid.[38] These intermediates were not isolated or characterized. Addition of acetonitrile (10 mL) led to formation of a bright blue precipitate. Elemental analysis of this compound was not satisfactory, although it appears to be a $CF_3SO_3^-$ salt of a molybdenum(II) acetonitrile complex. IR spectroscopy indicated strong CN and OH stretches as well as bands corresponding to uncoordinated $CF_3SO_3^-$ and residual acetate bands at 1615 cm^{-1} ($\nu_{asy}(CO_2)$) and 675 cm^{-1} ($\delta(CO_2)$). A band at 415 cm^{-1} may be $\nu(Mo_2)$. Slow evaporation of the filtrate obtained above resulted in formation of purple crystals of what is most likely **1**. The IR spectrum corresponded to **1** as did the elemental analysis, although the precipitate may have been contaminated with species such as $[Mo_2(O_2CCH_3)(CH_3CN)_x](CF_3SO_3)_3$, giving higher % S, % F, and % O. Anal. Calcd for $[Mo_2(O_2CCH_3)_2(CH_3CN)_4](CF_3SO_3)_2$: See above. Found: C, 21.33; H, 2.10; N, 6.23; S, 9.48; F, 15.48; Mo, 21.47; O (by difference), 23.91.

Experimental Methods. Elmental analyses were performed by the microanalytical laboratory of the University of Illinois. EPR spectra were recorded on a Varian E-9 instrument. $^{13}C\{^1H\}$ Fourier-transforming NMR spectra were recorded on a Varian Associates XL-100 FT spectrometer operating at 25.2 MHz. The ^{13}C chemical shifts were measured with respect to the nitrile carbon of CD_3CN (118.2 ppm relative to Me_4Si). ^1H NMR spectra were recorded on a Varian HR-220 NMR spectrometer equipped with a Nicolet Instrument Corp. TT-220 Fourier-transform accessory. Precision-grade tubes were used for the 220-MHz spectra so as to reduce spinning sidebands. All ^1H chemical shifts were measured relative to Me_4Si. Infrared spectra were recorded on a Perkin-Elmer 599B instrument. UV-vis spectra were recorded on a Cary 14 spectrometer with matched quartz 1.0-cm cells.

Registry No. 1, 89746-57-6; 2, 89746-59-8; $Mo_2(O_2CCH_3)_4$, 14221-06-8; $Rh_2(butyr)_4$, 56281-34-6; $Rh_2(butyr)_2^{2+}$, 89746-60-1; $[Mo_2(O_2CCH_3)_2(CH_3CN)_5](BF_4)_2$, 89746-61-2; $Rh_2(O_2CCH_2CH_2CH_3)_2S$, 89746-62-3; Mo, 7439-98-7; Rh, 7440-16-6.

---

(38) Subsequent to the submission of this paper, a report appeared (Mayer, J. M.; Abbott, E. H. *Inorg. Chem.* **1983**, *22*, 2774) in which this tan solid was reformulated as $[Mo_2(H_2O)_4(CF_3SO_3)_2](CF_3SO_3)_2$ synthesized under slightly different conditions. Addition of acetonitrile to this species led to isolation of a blue complex formulated as $[Mo_2(CH_3CN)_8](CF_3SO_3)_4$. The blue complex described in this work is most likely impure $[Mo_2(CH_3CN)_8](CF_3SO_3)_2$.

Contribution from the Department of Chemistry,
National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China

Nickel(II) Complexes of Diamino Diamides in Aqueous Solution

SI-HAN LIU and CHUNG-SUN CHUNG*

Received June 16, 1983

The basicity constants of *N,N'*-bis(β-carbamoylethyl)ethylenediamine, *N,N'*-bis(β-carbamoylethyl)trimethylenediamine, *N,N'*-bis(β-carbamoylethyl)-1,2-propylenediamine, and *N,N'*-bis(β-carbamoylethyl)-2-hydroxytrimethylenediamine were determined potentiometrically in 0.10 M $NaNO_3$ at 25.0 °C. The formation of nickel(II) complexes of these ligands and the Ni–O to Ni–N bond rearrangements at the two amide sites of these complexes were investigated quantitatively by potentiometric and spectrophotometric techniques under the same conditions. Electronic spectra of the nickel(II) complexes of these ligands and their deprotonated species formed in aqueous solution were measured and discussed.

Introduction

In previous studies of copper(II) complexes of *N,N'*-bis(β-carbamoylethyl)ethylenediamine, BCEN, and *N,N'*-bis(β-carbamolyethyl)trimethylenediamine, BCTN,[1,2] it was noted that copper(II), after complexation with each of these ligands, can induce ionization of the amide protons, and the Cu–O to Cu–N bond rearrangements at the two amide sites occur with an increase in pH. We now report an extension of the previous investigations to include a study of the interactions of four closely related diamino diamides, depicted in Chart I, with nickel(II). Like copper(II), nickel(II) can also induce ionization of the amide protons after combination with each of these ligands. The detailed stepwise reactions which follow the formation of the nickel(II) complex with each of these ligands and the Ni–O to Ni–N bond rearrangements at the two amide sites have now been studied by potentiometric and

---

(1) Wei, L.-W.; Chao, M.-S.; Chung, C.-S. *J. Chin. Chem. Soc. (Taipei)* **1979**, *26*, 145.

(2) Chao, M.-S.; Chung, C.-S. *J. Chem. Soc., Dalton Trans.* **1981**, 683.

0020-1669/84/1323-1803$01.50/0