Table I. Analytical, Infrared, and NMR Data for Some Rhenium Carbonyl Diketonate Complexes[a]

	% calcd			% found			τ_{CO}, cm^{-1} (in CH_2Cl_2)	τ, ppm (in acetone-d_6)
	C	H	P	C	H	P		
$[Re(CO)_3(acac)]_2(C_4H_{10}O_2)$	28.98	2.92		28.77	2.80		2040, 1925, 1890	acac: 8.04, 8.05, CH_3; 4.42, CH dme: 6.71, CH_3; 6.53, CH_2
$[Re(CO)_3(hfacac)]_2(C_4H_{10}O_2)$	22.99	1.16		22.28	1.35		2047, 1942, 1934	hfacac: 3.53, CH dme: 6.71, CH_3; 6.52, CH_2
$[Re(CO)_3(dpm)]_2(C_4H_{10}O_2)$	38.54	4.85		38.89	4.55		2041, 1908	dpm: 8.86, CH_3; 4.09, CH dme: 6.71, CH_3; 6.53, CH_2
$[Re(CO)_3(dbzm)]_2(C_4H_{10}O_2)$	44.60	3.00		43.97	2.94		2033, 1920, 1885	dbzm: 1.93, 2.50, C_6H_5; 2.92, CH dme: 6.73, CH_3; 6.55, CH_2
$[Re(CO)_3(trop)]_2(C_4H_{10}O_2)$	33.03	2.31		32.55	2.24		2031, 1910, 1882	trop: ~2.5, CH dme: 6.72, CH_3; 6.54, CH_2
$Re(CO)_3(acac)[CH_3P(C_6H_5)_2]$	44.28	3.54	5.44	44.95	3.31	5.33	2041, 1933, 1885	acac: 8.31, CH_3; 4.75, CH Phosphine: 7.93, CH_3; 2.52, C_6H_5

[a] Abbreviations: Hacac, 2,4-pentanedione; Hhfacac, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione; Hdpm, 2,2,6,6 tetramethyl-3,5-heptanedione; Hbdzm, 1,3-diphenyl-1,3-propanedione; Htrop, tropolone; dme, 1,2-dimethoxyethane.

$(CO)_3L_3$ complexes with a cis configuration and are not at all similar to the rarer trans derivatives.[5] Several $Mn(CO)_3(hfacac)L$ complexes also have similar infrared spectra in the CO stretching region.[2] The positions of the C—C and C—O stretching bands of the acetylacetonate ligand (1580 and 1528 cm^{-1}, respectively) are consistent only with the usual symmetrical coordination of the diketonate group through the two oxygen atoms.

The NMR spectra observed for these complexes are consistent with either bridged structure. The resonance signals for the protons on the diketonate ligands (Table I) have shifts typical of that observed for most carbonyl diketonate complexes. The protons on the 1,2-dimethoxyethane ligands have shifts very similar to the free molecule. The only unusual feature observed in the NMR spectra was seen in that of the acetylacetonate complex, where the methyl protons on the acetylacetonate ligand give rise to two closely spaced signals of nearly equal intensity while the γ proton is observed as a sharp singlet. Thus either one of the methyl groups on each of the two acetylacetonate ligands on the dinuclear complex is not equivalent to the other (as would be the case with the structure containing bridging diketonate groups) or both methyl groups on each ligand are equivalent but then the acetylacetonate ligands themselves are not. The latter possibility would require that the resonances for the γ protons would also have nearly the same chemical shifts which would not be too unexpected. Since the dimethoxyethane ligand is quite flexible and can exist in several conformations, either (or both) of the possibilities could exist in a structure containing a bridging dme ligand and cannot be distinguished with the present data.

When $[Re(CO)_3(acac)]_2(dme)$ reacts with an excess of methyldiphenylphosphine, the dimethoxyethane ligand is displaced and the mononuclear complex $Re(CO)_3(acac)[(C_6H_5)_2PCH_3]$ is formed. The reaction proceeds at room temperature and under these conditions no CO evolution takes place. Even with a large excess of phosphine ligand, no diphosphine complexes such as those formed from $Mn(CO)_4(hfacac)$[2] were observed. Infrared and NMR data (Table I) suggest a cis structure for this complex also.

Experimental Section

Analyses. Elemental analyses were carried out by the Analytical and Information Division of Exxon Research and Engineering Company. The results are given in Table I.

Spectra. Infrared spectra were obtained either on a Perkin-Elmer Model 521 infrared spectrometer or on a Beckman Model 20 infrared spectrometer. Spectra were obtained either as solutions in CH_2Cl_2 or as Nujol mulls between KBr plates. NMR spectra were obtained on a Varian Model A-60 NMR spectrometer usually as solutions in CD_3COCD_3.

Reagents. The preparation of the thallium(I) diketonate complexes was carried out by allowing exactly equivalent amounts of thallium(I) ethoxide to react with the β-diketones in benzene. Rhenium pentacarbonyl chloride was obtained by the method of Abel and Wilkinson.[6] All other reagents were purchased from commercial sources.

Preparation of $Re(CO)_3(diket)_2(dme)$ Complexes. A mixture of 3.61 g (0.01 mol) of $Re(CO)_5Cl$, an exactly equivalent amount of the thallium(I) diketonate salt, and 30 ml of dimethoxyethane was refluxed under N_2 for 72 hr. The solutions were filtered through a fine glass frit and the filtrate was evaporated to dryness on a rotary evaporator. The residue was washed several times with cold pentane and then redissolved in dimethoxyethane. The solution was again filtered and the filtrate was added to 150 ml of pentane precipitating the yellow solid complex. This was collected on a filter then dried by heating under vacuum (0.001 mm) at 50° for several hours. Yields were approximately 75%.

Preparation of $Re(CO)_3PCH_3(C_6H_5)_2(acac)$. Two grams each of $[Re(CO)_3(acac)]_2(dme)$ and $CH_3P(C_6H_5)_2$ were added to a flask containing 30 ml of acetone and were allowed to stand overnight in a N_2-filled drybox. The solution evaporated to a heavy oil during this period and the oil was washed several times with pentane. The residue was redissolved in acetone, the resulting solution was filtered, and the filtrate was added to 100 ml of pentane precipitating a yellow solid. This was collected on a filter and dried. The yield was 80%.

Registry No. $[Re(CO)_3(acac)]_2(C_4H_{10}O_2)$, 55222-36-1; $[Re(CO)_3(hfacac)]_2(C_4H_{10}O_2)$, 55222-35-0; $[Re(CO)_3(dpm)]_2(C_4H_{10}O_2)$, 55222-38-3; $[Re(CO)_3(dbzm)]_2(C_4H_{10}O_2)$, 55222-39-4; $[Re(CO)_3(trop)]_2(C_4H_{10}O_2)$, 55222-37-2; $Re(CO)_3(acac)[(CH_3P(C_6H_5)_2]$, 55124-59-9; $Re(CO)_5Cl$, 14099-01-5; 1,2-dimethoxyethane, 110-71-4.

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Contribution from the Institute of Chemistry, University of
Dortmund, Dortmund, West Germany, and the
Todd Wehr Chemistry Building, Marquette University,
Milwaukee, Wisconsin 53233

Metal Isotope Shifts and Normal-Coordinate Analysis of the $[^{58}Ni(^{92}MoS_4)_2]^{2-}$ Ion and Its ^{62}Ni and ^{100}Mo Analogs

E. Königer-Ahlborn, A. Müller,* A. D. Cormier, J. D. Brown, and K. Nakamoto

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Recently, we reported the preparation of novel coordination

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* To whom correspondence should be addressed at the University of Dortmund.

Table I. Comparison of Observed and Calculated Frequencies and Potential Energy Distribution in the $[Ni(MoS_4)_2]^{2-}$ Ion (cm^{-1})[a]

	Obsd				Calcd				
	ν	$\Delta\nu_{I}$	$\Delta\nu_{II}$	$\Delta\nu_{III}$	ν	$\Delta\nu_{I}$	$\Delta\nu_{II}$	$\Delta\nu_{III}$	Potential energy distribution[b]
B_{2u} ν_1	455.5	0.5	6.0	6.0	447.4	0.0	5.2	5.2	91% ν(Mo–S)
ν_2	323.8	4.7	0.3	5.0	323.4	4.9	0.0	4.9	89% ν(Ni–S)
ν_3	181.0	0.7	2.3	2.9	181.1	0.5	2.4	2.9	82% ρ_w(Mo=S) + 9% ν(Ni–S)
ν_4	50.0	0.5	0	0.5	50.0	0.6	0	0.6	71% δ(SNiS′) + 25% ν(Ni–S)
B_{3u} ν_5	494.0	0.0	6.0	6.0	484.6	0.0	3.8	3.8	89% ν(Mo=S)
ν_6	442.5	0.4	1.4	1.7	440.0	0.8	0.9	1.7	69% ν(Mo–S) + 25% ν(Ni–S)
ν_7	331.5	4.7	0	4.7	342.8	4.8	0.2	5.0	64% ν(Ni–S) + 15% ν(Mo–S) + 13% δ(SNiS)
ν_8	222.5	0.3	2.5	2.5	222.6	0.0	1.9	1.9	88% δ(Mo=S)
ν_9	179.5	1.2	2.0	3.3	180.4	2.4	1.2	3.6	57% δ(SNiS) + 36% δ(SMoS)

[a] $\Delta\nu_{I} = \nu(^{58}Ni^{92}Mo) - \nu(^{62}Ni^{92}Mo)$; $\Delta\nu_{II} = \nu(^{58}Ni^{92}Mo) - \nu(^{58}Ni^{100}Mo)$; $\Delta\nu_{III} = \nu(^{58}Ni^{92}Mo) - \nu(^{62}Ni^{100}Mo)$. The B_{1u} species are not listed because only one vibration [ν(Mo=S) at 513 cm^{-1} ($\Delta\nu_{II}$ = 7.0 cm^{-1})] could be determined with certainty. Our calculation (low-frequency separation) gives 503 cm^{-1} ($\Delta\nu_{II}$ = 7.6 cm^{-1}) for this band. [b] Key: ν, stretching; δ, bending; ρ_w, wagging.

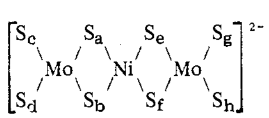
compounds of the type $[M(M'S_4)_2]^{2-}$ (M = Ni, Co, Fe, Zn; M′ = Mo, W) in which a complex ion ($M'S_4^{2-}$) coordinates to another metal (M).[1-5] The vibrational spectra of these trinuclear systems are of particular interest since they provide valuable information about the magnitude of interaction between the $M'S_4$ and MS_4 groups. In the present work, we measured the infrared spectra of the $[^{58}Ni(^{92}MoS_4)_2]^{2-}$ ion and its ^{62}Ni and ^{100}Mo analogs and carried out rigorous normal-coordinate analysis based on these isotopic frequencies. This is the first example of normal-coordinate analysis on a coordination compound containing two metal isotopes in one complex ion. Although we previously[6] reported the infrared spectra of $[^{64}Zn(^{92}MoS_4)_2]^{2-}$ and its ^{68}Zn and ^{NA}Mo (NA, natural abundance) analogs, normal-coordinate analysis was not carried out on these ions. Consequently, no detailed information such as that described here was obtained. It should be pointed out that the analog $[Fe(MoS_4)_2]^{2-}$ ion is one of the few inorganic systems containing the Fe–S–Mo bridge which is important as a model for nitrogen fixation.[7]

Experimental Section

$(PPh_4)_2[^{58}Ni(^{92}MoS_4)_2]$ and its ^{62}Ni and ^{100}Mo analogs were prepared on a milligram scale by the method described previously.[4] The Ni and Mo isotopes were purchased from Oak Ridge National Laboratory. All the isotopes were more than 90% pure. The infrared spectra were measured on a Perkin-Elmer Model 180 (4000–150 cm^{-1}) and a Hitachi Perkin-Elmer FIS-3 (400–33 cm^{-1}) far-infrared spectrophotometer. The Nujol mull technique with CsI plates (4000–200 cm^{-1}) or polyethylene plates (400–33 cm^{-1}) was employed for all compounds. The spectra below 550 cm^{-1} were recorded with a scanning speed of 4 cm^{-1}/min. Reproducibility of the spectra was checked by multiple scans over the desired frequency region. The frequency reading was calibrated by running the spectra of polystyrene, indene, 1,2,4-trichlorobenzene, and water vapor.

Results and Discussion

The structure of the $[Ni(MoS_4)_2]^{2-}$ ion is expected to be



where the Mo and Ni atoms are coordinated by four S atoms in tetrahedral and square-planar environments, respectively. Then the overall symmetry of the ion is regarded as D_{2h}. Previously, we[8] have carried out normal-coordinate analysis on the $[Ni(WS_4)_2]^{2-}$ ion. Since the detailed description of normal-coordinate analysis has already been given in this paper,[8] it will not be repeated here. Table I compares the observed and calculated frequencies and isotopic shifts for the B_{2u} and B_{3u} modes. Theoretical band assignments based on potential energy distribution are given in the last column of Table I.

The Urey–Bradley force constants[9] used are as follows (in units of mdyn/Å): K(Ni–S), 1.44; K(Mo–S_a), 2.30; K(Mo–S_c), 2.60; $H(S_aNiS_b)$, 0.25; $H(S_aNiS_e)$, 0.12; H(MoSNi), 0.02; $H(S_aMoS_b)$, 0.35; $H(S_aMoS_c)$, 0.37; $H(S_cMoS_d)$, 0.70; $F(S_a\cdots S_b)$, 0.06; $F(S_a\cdots S_e)$, 0.06; $F(Ni\cdots Mo)$, 0.06; $F(S_a\cdots S_c)$, 0.28; $F(S_c\cdots S_d)$, 0.48; κ, 0.08; $f(d_1, d_3)$, –0.24; $f(d_1, d_4)$, 0.31; $f(d_1, \gamma_1)$, 0.11; $f(d_1, \gamma_3)$, 0.20. The values of all these force constants are similar to those used previously for the $[Ni(WS_4)_2]^{2-}$ ion except K(Mo–S_a) and K(Mo–S_c). In addition, the following five new constants were necessary to fit the calculated isotopic shifts to those observed: $F(S_c\cdots Ni)$, 0.09; $f(d_1, r_1)$, –0.10; $f(r_1, r_2)$, –0.03; $f(r_1, R_1)$, –0.095; $f(R_1, \beta_1)$, –0.40. However, the physical meanings of these small interaction constants are difficult to assess without further study on similar systems.

Several important conclusions can be drawn from the present study.

(1) Within the experimental error, the additivity rule holds for the three types of isotopic shifts observed, namely, $\Delta_{I} + \Delta_{II} \approx \Delta_{III}$ (Table I). We have recently derived the additivity rule $\Delta\lambda_{I} + \Delta\lambda_{II} \approx \Delta\lambda_{III}$ ($\lambda = 4\pi^2c^2\nu^2$) using the first-order perturbation theory.[10] If these $\Delta\lambda$ values are small, it obviously gives the relation $\Delta\nu_{I} + \Delta\nu_{II} = \Delta\nu_{III}$. It should be emphasized that such a relationship has been proved for the first time by this work and that this rule will be very useful in checking the isotopic shifts of similar systems.

(2) The value of K(Ni–S) as well as the difference K(Mo–S_c) – K(Mo–S_a) gives a measure of the strength of the Ni–S bond. In the present case, these values are fairly large, indicating the formation of relatively strong coordinate bonds between the Ni(II) ion and the MoS_4 group.

(3) Some MoS_4 vibrations (ν_3) and ν_6) are coupled with the Ni–S stretching modes, and the Ni–S stretching (ν_7) is coupled with the Mo–S stretching mode. The most serious coupling between the MoS_4 and NiS_4 groups is seen in ν_9. Although the presence of these couplings was proved by the calculation of the potential energy distribution, the metal isotope data alone provide direct proof of such coupling when the substitution is made both on the Mo and Ni atoms.

(4) Finally, the present result also confirms the overall D_{2h} structure of the $[Ni(MoS_4)_2]^{2-}$ ion.

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Registry No. $[^{58}Ni(^{92}MoS_4)_2]^{2-}$, 54964-65-7; $[^{62}Ni(^{92}MoS_4)_2]^{2-}$, 54964-66-8; $[^{58}Ni(^{100}MoS_4)_2]^{2-}$, 54964-67-9; $[^{62}Ni(^{100}MoS_4)_2]^{2-}$, 54964-68-0.

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Webster Research Center, Webster, New York 14580

Synthesis and Characterization of New Iron–Dithiolene Complexes

Joel S. Miller

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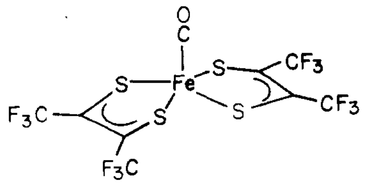
In the past decade several iron–carbonyl–dithiolene complexes have been characterized.[1] The reaction of iron pentacarbonyl with bis(perfluoromethyl)dithietene has been shown to form $\{Fe[S_2C_2(CF_3)_2]_2\}_2$,[2] **1**, and $[Fe(CO)_3]_nS_2C_2(CF_3)_2$, $n = 1$,[3] 2.[4] The reaction of **1** with Lewis bases has yielded pentacoordinate complexes of the $Fe[S_2C_2(CF_3)_2]_2$(base) type.[5] Herein is reported the parent member of the series: $Fe[S_2C_2(CF_3)_2]_2CO$, **2**. Compound **2** is prepared in quantitative yield by the evaporation of a filtered dichloromethane solution of **1** with a stream of carbon monoxide.[6a] The resulting deep blue complex exhibits a ν_{CO} absorption of 2059 cm^{-1} (KBr and CH_2Cl_2). This complex is thermally unstable with respect to loss of CO (equilibrium 1).[6b] Anal. Calcd:[9]

$$OCFe[S_2C_2(CF_3)_2]_2 = CO + {}^1/_2\{Fe[S_2C_2(CF_3)_2]_2\}_2 \qquad (1)$$

C, 20.16; H, 0.0; S, 23.92. Found: C, 19.70; H, 0.16; S, 23.87. Differential scanning calorimetry measurements reveal a broad endothermic peak at ~97.5° of 21 kcal/mol indicating CO loss over a broad temperature range, Figure 1. Reduction of **2** with hydrazine in dichloromethane yields an unstable red solution which does not exhibit a ν_{CO} absorbance in the 1750–2300-cm^{-1} region in dichloromethane indicating carbonyl extrusion. Attempts to isolate this red reduction product as the tetrabutylammonium salt lead to the isolation of $(Bu_4N)_2\{Fe[S_2C_2(CF_3)_2]_2\}_2$[2] suggesting instability of this red material. In dichloromethane **2** exhibits absorptions (log ϵ) at ~16,725 cm^{-1} (sh) (3.97), 21,420 cm^{-1} (3.38), 24,040 cm^{-1} (3.52), 30,490 cm^{-1} (3.56), 37,880 cm^{-1} (4.36). The absorptions are similar to that reported for $Fe[S_2C_2(CF_3)_2]_2L$ (L = $P(OPh)_3$, $AsPh_3$)[5] indicating the same electronic structure. By analogy to the X-ray structure of $Ph_3AsFe[S_2C_2(CF_3)_2]_2$,[7] **2** is proposed to have a square-pyramidal structure with an apical carbonyl group.



2

The reaction of **2** with monodentate phosphines results in the displacement of CO and the formation of $Fe[S_2C_2(CF_3)_2]_2PR_3$.[5] Polarographic measurements were thwarted by the decomposition of **2** in dichloromethane solutions of the supporting electrolyte. These results indicate the instability of **2** toward nucleophilic attack. Although crystals and solutions of **2** decompose in short periods of time at room temperatures (eq 1), **2** does not undergo photodecomposition with a high-pressure Hg lamp for 4 hr at −77°. Thus **2** is photoinert while being thermally unstable.

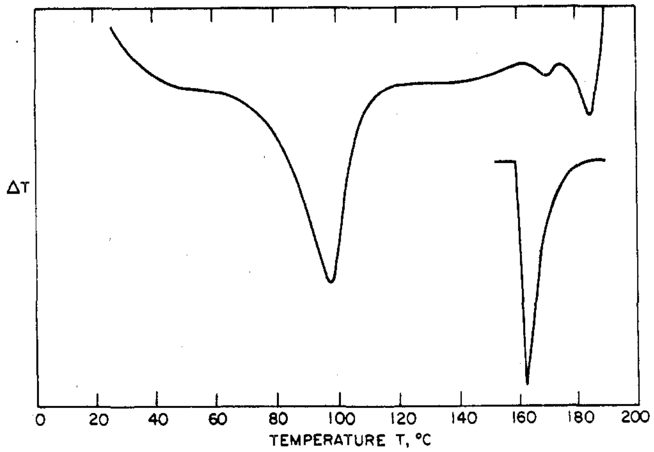


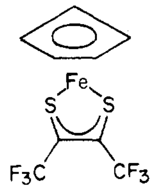
Figure 1. Differential scanning thermograms for 19.4 mmol of $Fe(CO)[S_2C_2(CF_3)_2]_2$ (top) and 0.217 mmol of In^0 calibrant (bottom).

Although η^5-$C_5H_5Fe[S_2C_2(CF_3)_2]$, **3**, has been characterized mass spectrally from the reaction product resulting from the reaction of cyclopentadienyl-μ-dicarbonyl-iron(I) dimer and bis(perfluoromethyl)dithietene[4] and reportedly exhibits a melting point of 150°,[1] no synthesis has yet been reported. Complex **3** has now been prepared by a rational synthesis from a reaction of cyclopentadienyl-μ_3-carbonyl-iron(I) tetramer[8] and bis(perfluoromethyl)dithietene (eq 2) in refluxing toluene

$$S_2C_2(CF_3)_2 + [Fe(\mu_3\text{-}CO)(\eta^5\text{-}C_5H_5)]_4 \rightarrow (F_3C)_2C_2S_2Fe(\eta^5\text{-}C_5H_5) \qquad (2)$$

for 12 hr. Recrystallization was effected from dichloromethene–*n*-hexane. The observed analysis is consistent with the formation. Anal. Calcd:[9] C, 31.14; H, 1.45; S, 18.47. Found: C, 30.95; H, 1.26; S, 19.06. A mass spectral parent ion was observed to be centered at *m/e* 347 (calcd 347 (^{56}Fe)). The solution molecular weight is 340 in *N,N*-dimethylformamide. A melting point of >300° was observed which is in sharp contrast with the previously cited melting point.[1] The infrared spectrum of **3** reveals characteristic cyclopentadienyl and dithiolene absorbances and indicates that bridging and terminal carbonyl groups are absent. These data suggest that **3** is monomeric and thus should possess one unpaired electron per metal site.

The structure of **3** is proposed to be similar to the diamagnetic complexes $(\eta^5\text{-}C_5H_5)Co(S_2C_2R_2)$ (R = CN,[10] CF_3[11,12]), $(\eta^5\text{-}C_5H_5)Ni[S_2C_2(CF_3)_2]$,[13] and $(\eta^5\text{-}C_5H_5)M[S_2C_2(CF_3)_2]$ (M = Rh, Ir).



3

Polarographic investigations show a single one-electron reduction wave at −0.44 V (vs. SCE electrode). Thus the reduced form of **3** was not readily isolated under ambient conditions.[1]