



Chelating and ligand-transfer studies of the complexes cis -[Mn(CO)₄(SeR)₂][−]: crystal structures of heterotrinnuclear [(CO)₄Mn(μ-SeMe)₂Ni(μ-SeMe)₂Mn(CO)₄] with a distorted square planar Ni^{II}–selenolate core and [PPN]₂[Cl₂Pd(μ-SePh)₂PdCl₂]

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Abstract

Trinuclear selenolate complexes [(CO)₄Mn(μ-SeR)₂Ni(μ-SeR)₂Mn(CO)₄] (R = Me, Ph) containing a distorted square planar Ni(Se)₄ core have been synthesized by the reaction of Ni(NO₃)₂·6H₂O/NiCl₂ with the chelating metalloligand cis -[PPN][Mn(CO)₄(SeR)₂] in MeCN. Their structures were elucidated on the basis of IR, UV–Vis, CV, and NMR spectra. X-ray crystallography confirmed the heterotrinnuclear structure in the solid state with a Ni^{II}–Se distance of 2.331(1) Å, and a Ni^{II}⋯Mn^I distance of 3.428(2) Å (average). The dependence of geometry on electron population and the larger Ni^{II}⋯Mn^I distances are adopted to rationalize the construction of the complex [(CO)₄Mn(μ-SeMe)₂Ni(μ-SeMe)₂Mn(CO)₄] with a distorted square planar Ni^{II}(Se)₄ core. Further reaction of cis -[PPN][Mn(CO)₄(SePh)₂] with PdCl₂ afforded [PPN]₂[Cl₂Pd(μ-SePh)₂PdCl₂]. Its structure has been determined. This investigation shows that cis -[Mn(CO)₄(SeR)₂][−] serves as a chelating metalloligand and selenolate ligand-transfer reagent. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Nickel complexes; Manganese complexes; Selenolate complexes; Heterometallic complexes

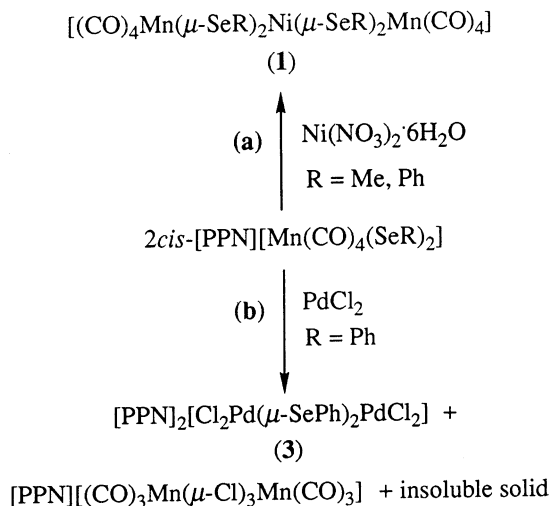
1. Introduction

The study of transition metal–selenolate, –telluroate chemistry has been actively pursued recently [1], motivated primarily by the bonding diversity [2], reactivity [3], potential use as precursors for M–Se materials [4], and the relevance of such complexes (e.g. Ni–chalcogenolate, Fe–Ni–chalcogenolate complexes) to biomimetic chemistry [5]. In particular, XAS analysis of acetyl coenzyme A synthase suggested that the nickel coordination was most consistent with distorted square planar geometry with Ni–S bonds of 2.21 Å [6], and the structure of the [NiFeSe] hydrogenase from *D. baculatus* revealed that the nickel is ligated to one Se

atom at 2.44 Å, one to two S–Cl atoms at 2.17 Å, and three to four N–O atoms at 2.06 Å [7].

Recent work in this laboratory has shown that cis -[PPN][Mn(CO)₄(ER)₂] (E = Te, Se; R = Ph, Me) complexes are useful in the syntheses of heterometallic chalcogenolate [(CO)₄Mn(μ-ER)₂Co(CO)(μ-ER)₃Mn(CO)₃] complexes with a unique Co^{III}–CO bond [8], and [(CO)₃M(μ-SePh)₃M'(μ-SePh)₃M(CO)₃]^{0/1−} (M = Fe, M' = Fe, Ni, Zn, Cd; M = Mn, M' = Co) with homoleptic hexaselenolatometal core [9]. A recent report on distorted square planar [Ni(CO)(SePh)₃][−] in preparations of the biomimetic nickel-site structure of [NiFeSe] hydrogenases and CO dehydrogenase has prompted us to synthesize heteronuclear Ni–M–selenolate complex [10]. Here we examined the reactivity of the manganese–selenolate species cis -[PPN][Mn(CO)₄(SeR)₂] (R = Me, Ph) by reacting it with NiCl₂ and

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Scheme 1.

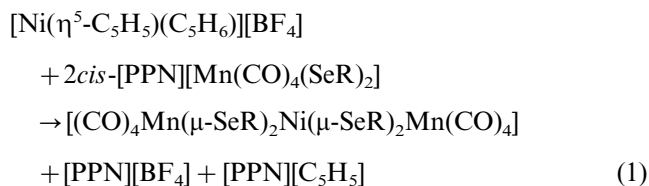
PdCl_2 individually. Specifically, the syntheses and characterization of the trinuclear $\text{Mn}^{\text{I}}\text{-Ni}^{\text{II}}\text{-selenolate}$ complexes containing a distorted square planar $\text{Ni}(\text{Se})_4$ core are described. In addition, the structure of the thermally stable $[\text{PPN}]_2[\text{Cl}_2\text{Pd}(\mu\text{-SePh})_2\text{PdCl}_2]$, employing $\text{cis-}[\text{Mn}(\text{CO})_4(\text{SePh})_2]^-$ as a chelating and intermetal ligand transfer reagent, is reported [9].

2. Results and discussion

As illustrated in Scheme 1(a), the reaction of $\text{cis-}[\text{Mn}(\text{CO})_4(\text{SeR})_2]^-$ ($\text{R} = \text{Me, Ph}$) and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (or NiCl_2) in a 2:1 molar ratio in MeCN yielded the neutral trinuclear complex $[(\text{CO})_4\text{Mn}(\mu\text{-SeR})_2\text{Ni}(\mu\text{-SeR})_2\text{Mn}(\text{CO})_4]$ ($\text{R} = \text{Me}$ (1), Ph (2)) by salt elimination

without the risk of adduct formation. The heterotrimetallic complex $[(\text{CO})_4\text{Mn}(\mu\text{-SeMe})_2\text{Ni}(\mu\text{-SeMe})_2\text{Mn}(\text{CO})_4]$ (1) which is soluble in common organic solvents like tetrahydrofuran (THF) and CH_2Cl_2 , displays no tendency to decompose under nitrogen at ambient temperature overnight. In contrast, significant decomposition was observed when stirring the neutral complex 2 THF solution at ambient temperature overnight. The carbonyl IR stretching frequency and an X-ray crystallographic structure determination confirmed the formation of neutral 1, and the ^1H , ^{13}C NMR spectra are consistent with the presence of low-spin d^8 Ni^{II} and octahedrally coordinated d^6 Mn^{I} . The neutral complex 1 appears to have no precedent in nickel–manganese–selenolate chemistry.

Additionally, when $\text{cis-}[\text{Mn}(\text{CO})_4(\text{SeR})_2]^-$ ($\text{R} = \text{Me, Ph}$) was reacted in stoichiometric proportions with $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_5\text{H}_6)]^+$ (obtained from protonation ($[\text{HBF}_4]$) of Cp_2Ni) in acetonitrile under N_2 , the neutral trinuclear complex 1 was also obtained after being separated from $[\text{PPN}][\text{BF}_4]$, and $[\text{PPN}][\text{C}_5\text{H}_5]$ (Eq. (1)).



The electrochemistry of complex 1, measured in THF with 0.05 M $[\text{N}^n\text{Bu}_4][\text{PF}_6]$ as the supporting electrolyte, shows two reversible processes which are tentatively assigned as $\text{Ni}^{\text{III/II}}$ and $\text{Ni}^{\text{II/I}}$ couples individually. The electrochemically reversible $\text{Ni}^{\text{III/II}}$ and $\text{Ni}^{\text{II/I}}$ couples are centered at 0.23 and -0.14 V (versus $\text{Ag}|\text{AgCl}$) respectively.

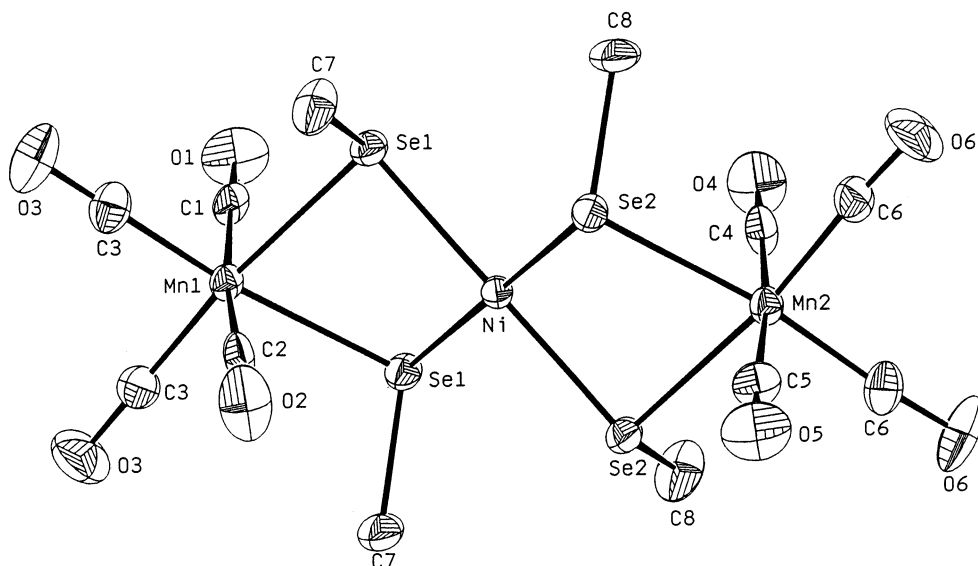


Fig. 1. ORTEP drawing and labeling scheme of the neutral $[(\text{CO})_4\text{Mn}(\mu\text{-SeMe})_2\text{Ni}(\mu\text{-SeMe})_2\text{Mn}(\text{CO})_4]$ with thermal ellipsoids drawn at the 30% probability level.

Table 1
Selected bond distances (Å) and angles (°) for **1** and **3**

1			
Ni–Se(1)	2.337(1)	Mn(1)–Se(1)	2.485(2)
Ni–Se(2)	2.326(1)	Mn(2)–Se(2)	2.480(2)
Se(1)–Ni–Se(1)	84.77(6)	Se(2)–Ni–Se(2)	84.77(6)
Se(1)–Ni–Se(2)	95.23(4)	Se(1)–Ni–Se(2)	180.0
Se(1)–Mn(1)–Se(1)	78.70(6)	Se(2)–Mn(2)–Se(2)	78.43(6)
Ni–Se(1)–Mn(1)	90.19(5)	Ni–Se(2)–Mn(2)	91.31(5)
3			
Pd–Se	2.335(1)	Pd–Cl(1)	2.362(2)
Pd–Se	2.389(1)	Pd–Cl(2)	2.303(2)
Se–Pd–Se	82.19(3)	Se–Pd–Cl(1)	92.22(5)
Se–Pd–Cl(2)	172.86(5)	Se–Pd–Cl(1)	174.13(5)
Se–Pd–Cl(2)	90.82(5)	Cl(1)–Pd–Cl(2)	94.81(6)
Pd–Se–Pd	97.81(3)		

The molecular structure of **1** is depicted in Fig. 1; selected bond distances and angles are given in Table 1. Nickel is best described as existing in a distorted square planar coordination environment surrounded by four bridging methylselenolates with Se(1)–Ni–Se(1) 84.77(6), Se(1)–Ni–Se(2) 95.23(4) and Se(1)–Ni–Se(2) 179.92(7)°. The complex **1** exhibits a shorter Ni^{II}–Se distance (average 2.331(1) Å) than the Ni^{II}–Se distances reported in tetrahedral [Ni(SePh)₄]²⁻ (Ni–Se_{av} = 2.401(3) Å) [11], five-coordinate [Ni(DAPA)(SePh)₂] (Ni–Se_{av} = 2.420(1) Å) [12], but longer than those observed for planar [NiSe(CH₂)₂N(Me)(CH₂)₂Se]₂ (average Ni^{II}–Se = 2.295(6) Å) [13], [Ni(CO)(SePh)₃]⁻ (average Ni^{II}–Se = 2.317(2) Å) [10], [(C₄H₉)₄N]₂[Ni(ddd)₂] (ddd = 5,6-dihydro-1,4-dithiin-2,3-diselenolate, Ni–Se_{av} = 2.267(3) Å) [14]. The mean Mn^I–Se bond of length 2.482(2) Å is comparable with terminal Mn^I–Se of 2.526(4) Å in *cis*-[Mn(CO)₄(SePh)₂]⁻ [8b]. It is interesting that here Ni^{II} when coordinated by four μ²-selenolates has a square planar geometry whereas the monomeric [Ni(SePh)₄]²⁻ (E = Se) complexes have distorted tetrahedral structures [11]. Further examination shows that there is no significant Ni^{II}⋯Mn^I bonding (Ni⋯Mn(1) 3.417(2) and Ni⋯Mn(2) 3.438(2) Å) in complex **1**, but the four-membered NiSe₂Mn rings are decidedly bent with a dihedral angle between MnSe₂ and NiSe₂ planes of 39.69°. In contrast, the analogous heterotrimeric Ni–Nb–thiolate complex [Cp₂Nb(μ-SMe)₂]₂Ni²⁺ has the Ni⁰ atom in an approximately tetrahedral arrangement of the bridging thiolates, and Ni⁰–Nb^{IV} metal–metal bonds [15]. Here the dependence of geometry on electron population and the longer Ni^{II}⋯Mn^I distances are adopted to rationalize the construction of complex **1** with a square planar Ni^{II}–selenolate core [15].

In comparison, the addition of two equiv. of *cis*-[Mn(CO)₄(SePh)₂]⁻ to a MeCN solution of PdCl₂

under N₂ led to the isolation of red [PPN]₂[Cl₂Pd(μ-SePh)₂PdCl₂] (**3**), the known [PPN][Mn(CO)₃(μ-Cl)₃Mn(CO)₃], and presumably polymeric Pd(SePh)_n (Scheme 1(b)). The complex **3** is soluble and stable in MeCN, and easily crystallized from MeCN/diethyl ether at –15°C. The most likely explanation for this result (Scheme 1(b)) is that *cis*-[Mn(CO)₄(SePh)₂]⁻ was employed as an intermetal ligand transfer reagent. Also, the ¹H NMR spectrum of **3** shows the expected signals (δ 7.4–7.7 (m) ppm (Ph) (CD₃CN)) for the phenyl ligands involved and displays characteristics of diamagnetic d⁸ Pd^{II} species.

The definitive assignment of the structure of complex **3** was obtained by X-ray crystallography. An ORTEP [16] plot of the anionic dimeric compound with its numbering scheme is shown in Fig. 2, selected bond distances and angles are given in Table 1. The core geometry of **3** is best described as a Pd₂Se₂ distorted planar square. Each Pd^{II} atom makes four bonds, two to selenium atoms of two bridging phenylselenolates and two to two terminal chloride atoms. Two bridging phenylselenolates and two terminal chloride ligands define the distorted square planar geometry of each Pd^{II} atom (angles Se–Pd–Se 82.19(3), Se–Pd–Cl(1) 92.22(5), Se–Pd–Cl(2) 172.86(5)°). The Pd(II)–Se bond of distance 2.362(1) Å (average) may be compared with Pd–Se distances in known compounds [Pd{N(SePh)₂–Se, Se'}₂] (2.446(2) Å average) [17], and [Pd(PhSeN(4-CH₃C₆H₄)CN)₂(PPh₃)] (2.375(1) Å) [18].

In these investigations, the complexes *cis*-[Mn(CO)₄(SeR)₂]⁻ exhibit a unique coordination be-

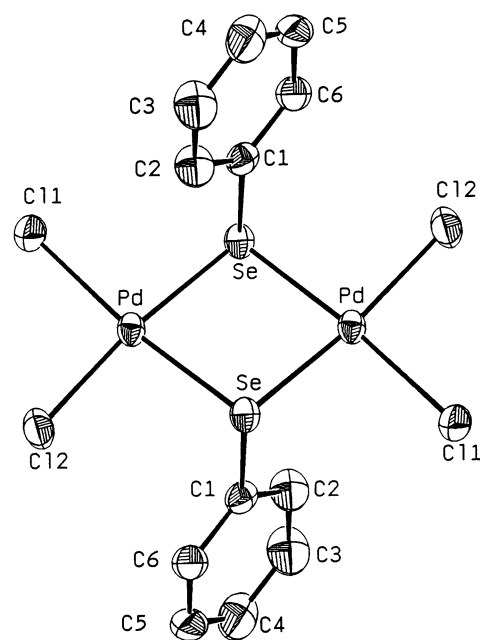


Fig. 2. ORTEP drawing and labeling scheme of the [Cl₂Pd(μ-SePh)₂PdCl₂]²⁻ with thermal ellipsoids drawn at the 30% probability level.

havior toward the divalent nickel ion, and act as potential chelating metallo ligands; the chelating/ligand-transfer properties of these Mn^I-chalcogenolate complexes offer novel routes toward heterometallic chalcogenolate species.

3. Experimental

Manipulations, reactions, and transfers of samples were conducted under nitrogen according to standard Schlenk techniques or in a glovebox (argon gas). Solvents were distilled under nitrogen from appropriate drying agents (diethyl ether from CaH₂; acetonitrile from CaH₂-P₂O₅; hexane and THF from Na-benzophenone) and stored in dried, N₂-filled flasks over 4 Å molecular sieves. A nitrogen purge was used on these solvents before use and transfers to reaction vessels were via stainless-steel cannula under N₂ at a positive pressure. The reagents manganese decacarbonyl, dimethyl diselenide, diphenyl diselenide, bis(triphenylphosphoranylidene)ammonium chloride (PPN), Ni(NO₃)₂·6H₂O, NiCl₂ (Aldrich) were used as received. Infrared spectra were recorded on a Bio-Rad FTS-185 and FTS-7 FTIR spectrometer with sealed solution cells (0.1 mm) and KBr windows, NMR spectra on a Bruker AC 200 spectrometer, ¹H and ¹³C chemical shifts being relative to tetramethylsilane and UV-Vis spectra on a GBC 918 spectrophotometer. Cyclic voltammetric measurements were performed on a BAS-100B electrochemical analyzer, using glassy carbon as the working electrode, and [NⁿBu₄][PF₆] as the supporting electrolyte. Analyses of carbon, hydrogen and nitrogen were obtained with a CHN analyzer (Heraeus).

3.1. Preparation of [(CO)₄Mn(μ-SeR)₂Ni(μ-SeR)₂Mn(CO)₄] (R = Me (**1**), Ph (**2**))

A solution containing *cis*-[PPN][Mn(CO)₄(SeMe)₂] (0.4 mmol, 0.358 g) [8b] and Ni(NO₃)₂·6H₂O (0.2 mmol, 0.058 g) or NiCl₂ in acetonitrile (10 ml) was stirred under nitrogen at room temperature. After stirring of the reaction solution for 30 min, the brown solution accompanied with dark brown precipitate was formed. The brown solution was removed under positive N₂, then the dark brown solid was washed with MeCN twice, and dried under vacuum. The yield was 0.106 g (69%) of a dark brown solid. Diffusion of hexane into [(CO)₄Mn(μ-SeMe)₂Ni(μ-SeMe)₂Mn(CO)₄] THF solution at -15°C for 4 weeks led to formation of dark brown crystals of [(CO)₄Mn(μ-SeMe)₂Ni(μ-SeMe)₂Mn(CO)₄] suitable for X-ray crystallography. IR (THF): ν (CO) 2063 m, 1990 vs, 1977 sh and 1952 m cm⁻¹ (IR (THF): ν (CO) 2067 m, 1995 vs, 1987 sh and 1960 m cm⁻¹ for R = Ph). ¹H NMR (CD₂Cl₂): δ 1.74

(s, br) ppm (Me). ¹³C NMR (CD₂Cl₂): δ 5.4 (br) ppm (Me). Absorption spectrum (THF): λ_{max} nm (ε M⁻¹ cm⁻¹) 663(332), 518(1194), 432(4904), 383(5995), 307(9051). Anal. Calc. for C₁₂H₆O₈Se₄NiMn₂: C, 18.75; H, 1.57. Found: C, 18.93; H, 1.76%.

3.2. Reaction of *cis*-[PPN][Mn(CO)₄(SePh)₂] and PdCl₂

A solution of *cis*-[PPN][Mn(CO)₄(SePh)₂] (0.4 mmol, 0.407 g) in MeCN (10 ml) was stirred with PdCl₂ (0.2 mmol, 0.036 g) overnight at ambient temperature, resulting in the formation of an orange-red solution and the solvent-insoluble brown-red solid. The orange-red solution was transformed into another flask, and then THF (10 ml) was added to precipitate the red solid [PPN]₂[Cl₂Pd(μ-SePh)₂PdCl₂] (**3**) (31%), and the orange solution (MeCN-THF) solution identified as the known [PPN][(CO)₃Mn(μ-Cl)₃Mn(CO)₃] by IR (IR: ν (CO) 2017 m and 1927 s cm⁻¹ (THF); 2043 m, 1955 s and 1932 s cm⁻¹ (MeCN)). Diffusion of diethyl ether into [PPN]₂[Cl₂Pd(μ-SePh)₂PdCl₂] MeCN solution at -15°C led to red crystals of [PPN]₂[Cl₂Pd(μ-SePh)₂PdCl₂]·4MeCN suitable for X-ray diffraction. ¹H NMR (CD₃CN): δ 7.4–7.7 (m) ppm (Ph). Anal. Calc. for C₈₄H₇₀N₂P₄Cl₄Se₂Pd₂: C, 57.852; H, 4.046; N, 1.606. Found: C, 57.744; H, 4.124; N, 1.587%.

4. Crystallography

Crystallographic data for complexes **1**, and **3** are collected in Table 2 and in Section 5. All crystals were chunky: **1**, dark brown, ca. 0.40 × 0.50 × 0.50 mm; **3**, red, 0.25 × 0.30 × 0.30 mm. Each was mounted on a glass fiber and quickly coated in epoxy resin. The unit-cell parameters were obtained by the least-square refinement from 25 reflections with 2θ between 18.40 and 30.34° for **1**, 19.00 < 2θ < 32.72° for **3**. Diffraction measurements for complexes **1** and **3** were carried out at 25°C on a Nonius CAD 4 diffractometer with graphite-monochromated Mo Kα radiation (λ 0.7107 Å) employing the θ–2θ scan mode [19]. A ψ-scan absorption correction was made. The NRCC-SDP-VAX package of programs was employed and atomic scattering factors were from Ref. [20].

5. Supplementary material

Tables of crystal data and experimental conditions for the X-ray studies, atomic coordinates and B_{eq} values, bond lengths and angles for [(CO)₄Mn(μ-SeMe)₂Ni(μ-SeMe)₂Mn(CO)₄], and [PPN]₂[Cl₂Pd(μ-SePh)₂PdCl₂]·4MeCN (11 pages) are available from the authors on request.

Table 2
Crystallographic data of complexes **1** and **3** · 4MeCN

	1	3
Chemical formula	C ₁₂ H ₁₂ O ₈ Mn ₂ NiSe ₄	C ₉₂ H ₈₂ N ₆ P ₄ Cl ₄ Pd ₂ Se ₂
Formula weight	768.64	1908.11
Crystal system	orthorhombic	monoclinic
Space group	<i>Pnma</i>	<i>P2₁/c</i>
<i>a</i> (Å)	12.775(5)	11.120(3)
<i>b</i> (Å)	13.532(5)	12.304(4)
<i>c</i> (Å)	12.776(5)	31.397(5)
β (°)		91.852(16)
λ (Å) (Mo K α)	0.7107	0.7107
<i>V</i> (Å ³)	2208.7(15)	4293.5(18)
<i>Z</i>	4	2
<i>D</i> _{calc} (g cm ⁻³)	2.312	1.476
<i>F</i> (000)	1450	1925
μ (cm ⁻¹)	84.92	14.95
<i>T</i> (°C)	25	25
<i>R</i> ^a	0.033	0.037
<i>R</i> _w ^b	0.031	0.037
Goodness-of-fit ^c	1.41	1.45

$$^a R = \sum |F_o - F_c| / \sum F_o$$

$$^b R_w = [\sum w(F_o - F_c)^2 / \sum wF_o^2]^{1/2}$$

^c GOF = $[\sum [w(F_o - F_c)]^2 / (M - N)]^{1/2}$ where *M* is the number of reflections and *N* is the number of parameters.

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References

- [1] (a) J. Arnold, *Prog. Inorg. Chem.* 43 (1995) 353. (b) W.A. Howard, T.M. Trnka, G. Parkin, *Inorg. Chem.* 34 (1995) 5900. (c) M. Bochmann, G.C. Bwembya, R. Grinter, A.K. Powell, K.J. Webb, M.B. Hursthouse, K.M.A. Malik, M.A. Mazid, *Inorg. Chem.* 33 (1994) 2290. (d) J.J. Ellison, K. Ruhlandt-Senge, H.H. Hope, P.P. Power, *Inorg. Chem.* 34 (1995) 49.
- [2] (a) M. Berardini, T.J. Emge, J.G. Brennan, *Inorg. Chem.* 34 (1995) 5327. (b) A.K. Verma, T.B. Rauchfuss, *Inorg. Chem.* 34 (1995) 6199. (c) M.B. Bochmann, K.J. Webb, M.B. Hursthouse, M. Mazid, *J. Chem. Soc., Dalton Trans.* (1991) 2317. (d) W.-F. Liaw, C.-H. Lai, S.-J. Chiou, Y.-C. Horng, C.-C. Chou, M.-C. Liaw, G.-H. Lee, S.-M. Peng, *Inorg. Chem.* 34 (1995) 3755. (e) W.-F. Liaw, M.-H. Chiang, C.-H. Lai, S.-J. Chiou, G.-H. Lee, S.-M. Peng, *Inorg. Chem.* 33 (1994) 2493. (f) W.-F. Liaw, S.-J. Chiou, G.-H. Lee, S.-M. Peng, *Inorg. Chem.* 37 (1998) 1131.
- [3] (a) C.P. Gerlach, V. Christou, J. Arnold, *Inorg. Chem.* 35 (1996) 2758. (b) A.R. Strzelecki, C.C. Likar, B.A. Helsel, T. Utz, M.C. Lin, P.A. Bianconi, *Inorg. Chem.* 33 (1994) 5188. (c) B. Kersting, B. Krebs, *Inorg. Chem.* 33 (1994) 3886. (d) P.M. Boorman, H.-B. Kraatz, M. Parvez, T. Ziegler, *J. Chem. Soc., Dalton Trans.* (1993) 433.
- [4] (a) Y. Cheng, T.J. Emge, J.G. Brennan, *Inorg. Chem.* 35 (1996) 342. (b) M.G. Kanatzidis, S. Huang, *Coord. Chem. Rev.* 130 (1994) 509. (c) J.G. Brennan, T. Siegrist, P.J. Carroll, S.M. Stuczynski, L.E. Brus, M.L. Steigerwald, *J. Am. Chem. Soc.* 111 (1989) 4141. (d) M.L. Steigerwald, C.R. Sprinkle, *J. Am. Chem. Soc.* 109 (1987) 7200. (e) M.A. Ansari, J.C. Bollinger, J.A. Ibers, *J. Am. Chem. Soc.* 32 (1993) 1746. (f) C.J. Warren, D.M. Ho, A.B. Bocarsly, R.C. Haushalter, *J. Am. Chem. Soc.* 115 (1993) 6416.
- [5] (a) S.W. Ragsdale, in: H.L. Drake (Ed.), *Acetogenesis*, Chapman and Hall, New York, 1994. (b) M.A. Halcrow, G. Christou, *Chem. Rev.* 94 (1994) 2421. (c) A.F. Kolowicz, *Prog. Inorg. Chem.* 41 (1994) 493. (d) C. Zhou, L. Cai, R.H. Holm, *Inorg. Chem.* 35 (1996) 2767. (e) S.A. Mirza, R.O. Day, M. Maroney, *J. Inorg. Chem.* 35 (1996) 1992. (f) C.M. Goldman, M.M. Olmstead, P.K. Mascharak, *Inorg. Chem.* 35 (1996) 2752. (g) C.A. Grapperhaus, M.Y. Daresbourg, L.W. Sumner, D.H. Russell, *J. Am. Chem. Soc.* 118 (1996) 1791. (h) J.D. Franolic, M. Millar, S.A. Koch, *Inorg. Chem.* 34 (1995) 1981.
- [6] S.P. Cramer, M.K. Eidsness, W.-H. Pan, T.A. Morton, S.W. Ragsdale, D.V. DerVartanian, L.G. Lungdahl, R.A. Scott, *Inorg. Chem.* 26 (1987) 2477.
- [7] M.K. Eidsness, R.A. Scott, B.C. Prickril, D.V. DerVartanian, J. LeGall, I. Moura, J.J.G. Moura, H.D. Peck Jr., *Proc. Natl. Acad. Sci. USA* 86 (1989) 147.
- [8] (a) W.-F. Liaw, D.-S. Ou, Y.-S. Li, W.-Z. Lee, C.-Y. Chuang, Y.-P. Lee, G.-H. Lee, S.-M. Peng, *Inorg. Chem.* 34 (1995) 3747. (b) W.-F. Liaw, C.-Y. Chuang, W.-Z. Lee, C.-K. Lee, G.-H. Lee, S.-M. Peng, *Inorg. Chem.* 35 (1996) 2530.
- [9] (a) W.-F. Liaw, W.-Z. Lee, C.-Y. Wang, G.-H. Lee, S.-M. Peng, *Inorg. Chem.* 36 (1997) 1253. (b) W.-F. Liaw, C.-H. Chen, C.-M. Lee, G.-Y. Lin, C.-Y. Ching, G.-H. Lee, S.-M. Peng, *J. Chem. Soc., Dalton Trans.* (1998) 353.
- [10] W.-F. Liaw, Y.-C. Horng, D.-S. Ou, C.-Y. Ching, G.-H. Lee, S.-M. Peng, *J. Am. Chem. Soc.* 119 (1997) 9299.
- [11] C.M. Goldman, M.M. Olmstead, P.K. Mascharak, *Inorg. Chem.* 35 (1996) 2752.
- [12] (a) N. Baidya, B.C. Noll, M.M. Olmstead, P.K. Mascharak, *Inorg. Chem.* 31 (1992) 2999. (b) N. Baidya, M.M. Olmstead, P.K. Mascharak, *J. Am. Chem. Soc.* 114 (1992) 9666.
- [13] S.B. Choudhury, M.A. Pressler, S.A. Mirza, R.O. Day, M. Maroney, *Inorg. Chem.* 33 (1994) 4831.
- [14] H. Fujiwara, E. Arai, H. Kobayashi, *J. Chem. Soc., Chem. Commun.* (1997) 837.
- [15] (a) K. Prout, S.R. Critchley, G.V. Rees, *Acta Crystallogr., Sect. B*, 30 (1974) 2305. (b) P.J. Blower, J.R. Dilworth, *Coord. Chem. Rev.* 76 (1987) 121.
- [16] C.K. Johnson, ORTEP, Report ORNL-5138, Oak ridge National Laboratory, Oak Ridge, TN, 1976.
- [17] P. Bhattacharyya, J. Novosad, J. Phillips, A.M.Z. Slawin, D.J. Williams, J.D. Woollins, *J. Chem. Soc., Dalton Trans.* (1995) 1607.
- [18] T. Chivers, K. McGregor, M. Parvez, *Inorg. Chem.* 33 (1994) 2364.
- [19] A.C.T. North, D.C. Philips, F.S. Mathews, *Acta Crystallogr., Sect. A* 24 (1968) 351.
- [20] (a) E.J. Gabe, Y. LePage, J.P. Chartrand, F.L. Lee, P.S. White, *J. Appl. Crystallogr.* 22 (1989) 384. (b) *International Tables for X-Ray Crystallography*, vol. 4, Kynoch Press, Birmingham, 1974.