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A New Synthetic Pathway for Tris-μ-disulfido-μ_3-thio-triangulo-trimolybdenum(IV) Complexes: Preparation, Characterization and Structure of $[Mo_3S(S_2)_3(OOC{-}CHS{-}CH_2{-}COOH)_3]^{2-}$

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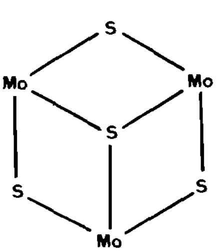
Abstract

A new synthetic pathway for complexes containing the polynuclear core $[Mo_3S_7]^{4+}$ is described: $[Mo_3S_7(S_2)_3]^{2-}$ reacts with HBr to $[Mo_3S_7Br_6]^{2-}$ which seems to be a useful intermediate for further ligand substitution. A new complex with mercapto-succinic acid $C_4H_6O_4S$ (H_3msa) as ligand could be prepared. ^{1}H NMR and ^{13}C NMR spectra and X-ray crystal structure analysis are in agreement with the bidentate coordination of mercapto-succinic acid, where S^- and COO^- are bound to the same molybdenum atom forming a five-membered ring. A monoclinic crystal, space group *C*2, of the composition $[C_{18}H_{30}N_3]_2[Mo_3S_7(Hmsa)_3][Mo_3S_7(Hmsa)_2(msa)]\cdot Br\cdot 6H_2O$ was used for X-ray diffraction. The cell parameters are $a = 21.968(7)$, $b = 13.423(13)$, $c = 18.828(3)$ Å, $\beta = 94.23°$, $Z = 2$, $D_c = 1.606$ g/cm^3, $\mu(\text{Mo K}\alpha) = 13.51$ cm^{-1}.

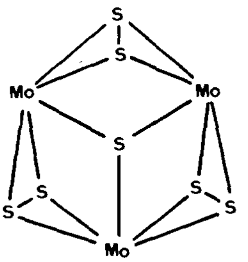
$[Mo_3S_7(Hmsa)_3]^{2-}$ is stable in water and air, and it can be precipitated from aqueous solution by the addition of large three-fold charged cations. It can be deprotonated reversibly to $[Mo_3S_7(msa)_3]^{5-}$ in water. The p*K* values are 3.95, 4.41, 5.02 (1 M KCl, 25 °C). To confirm the above described procedure as a useful approach for $[Mo_3S_7]^{4+}$ complexes, a similar compound with 2-mercapto-benzoic acid was also prepared.

Introduction

In the past 15 years, considerable attention has been given to the study of polynuclear molybdenum complexes due to their importance in catalytic and enzymatic processes. A striking quality of molybdenum is its ability to form oligonuclears with 2 to 6 Mo atoms in medium oxidation state (II to V) with significant Mo–Mo bonds [1, 2]. In our laboratories, interest was mainly focussed on trinuclear Mo(IV)–S complexes of the triangulo type. Two distinct structures of molybdenum–sulfur cores are known:



$[Mo_3S_4]^{4+}$



$[Mo_3S_7]^{4+}$

In both cases, the three Mo atoms form a regular triangle capped by a single μ_3-sulfur atom. The three Mo(IV) atoms are either bridged by three sulfido or disulfido entities. Interconversion of the two forms is well known for some Mo_3S_4/Mo_3S_7 couples. Mo_3S_7 complexes react easily to Mo_3S_4 derivatives with sulfur abstracting agents such as CN^- or triphenylphosphine [3–5]. The inverse reaction occurs in the presence of sulfur donating agents like S_8.

A large variety of $[Mo_3S_4]^{4+}$ complexes with H_2O [6, 7], CN^- [8], phosphines [9, 10], cyclopentadienyl [11], mercaptanes [5], dithiophosphinates [12], dithiophosphates [13], amino-polycarboxylates [14, 15], and aliphatic amines [16] as additional ligands are described in the literature. In the $[Mo_3S_4]^{4+}$ unit, sulfur can be replaced by oxygen. Compounds of $Mo_3S_xO_{4-x}$ are known where *x* ranges from 0 to 4 [17]. For $[Mo_3S_7]^{4+}$ however, no oxygen analogue appears to be known and only a relatively small number of complexes have been mentioned yet: $Mo_3S_7Cl_4$, a polymer containing the $Mo_3S_7Cl_6$ unit with 4 bridging Cl^- ligands was already described in 1974 [18]; a similar bromine

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analogue also seems to exist [19], and the monomer $[Mo_3S_7Cl_6]^{2-}$ was prepared some years ago [20, 21]. $[Mo_3S_{13}]^{2-}$, the 'Müller compound', contains three S_2^{2-} as terminal ligands [22]. Derivatives with dithiophosphates [23], dithiophosphinates [24] and dithioglycolate [5] were described recently.

Different synthetic pathways have been reported for the preparation of $[Mo_3S_7]^{4+}$ complexes, using such different Mo sources as $Mo(CO)_6$ and $[Mo_7O_{24}]^{6-}$. It seems however, that there is no obvious strategy for the synthesis of further $[Mo_3S_7]^{4+}$ complexes. In this work, a new synthetic pathway for complexes with bidentate ligands, containing sulfur and oxygen as ligand atoms, is given. Two new negatively charged, water soluble complexes of remarkable stability against air, aqueous acid and base, and a method to precipitate crystalline solids of $[Mo_3S_7]^{4+}$ complexes from aqueous solutions are described.

Experimental

Preparation of Mo_3S_7 Complexes

$(NH_4)_2Mo_3S_{13}$ (1)

This was prepared according to the method described in ref. 25. A total of 12 g $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was dissolved in 60 ml of hot water and 240 ml of a saturated solution of $(NH_4)_2S_2$ was added. The deep red solution was allowed to stand for 20 h at 90 °C. After filtration, 6.2 g (37%) of red crystals could be isolated.

$(N(C_2H_5)_4)_2Mo_3S_7Br_6\cdot\frac{1}{3}CH_3CN$ (2)

A total of 500 mg of 1 was suspended in 20 ml chloroform and 5 ml of concentrated hydrobromic acid (62%) were added. The suspension was kept under reflux for 2 h and then the chloroform layer was separated. The water fraction was filtered and the remaining solid was washed with water several times. The brown aqueous solution was heated and a saturated aqueous solution of tetraethylammoniumbromide was added. A yellow, crystalline solid was obtained. Recrystallization from acetonitrile/ether gave 600 mg (70%) of 2.

Anal. Calc. for $C_{16}H_{40}N_2Br_6Mo_3S_7\cdot\frac{1}{3}CH_3CN$: Mo, 22.75; C, 15.81; H, 3.26; N, 2.57; Br, 37.88. Found: Mo, 22.64; C, 15.62; H, 3.15; N, 2.52; Br, 37.8%.

$[Mo_3S_7(Hmsa)_3]^{2-}$ (3)

A total of 2 g of 2 was suspended in 200 ml acetonitrile and the mixture heated to 70 °C. Upon addition of 4 g H_3msa a clear orange solution resulted which was stirred for about 10 min. Triethylamine (3 g), dissolved in 25 ml acetonitrile, was added dropwise. After the addition of about 50% of the base, the product began to precipitate. The suspension was stirred for another hour at 70 °C and then allowed to cool to room temperature. The solid obtained was a mixture of the triethylammonium and tetraethylammonium salt of complex 3. Yield: 1.76 g.

$Mo_3S_7(mba)_3]^{2-}$ (4)

A total of 5 g of 2 was mixed with 4 g of H_2mba and 8 g of triethylamine as described for the preparation of 3. Yield: 4.0 g of a red–orange solid.

Precipitation from aqueous solution

A total of 30 mg of 3 or 4 was dissolved in 50 ml hot water. Addition of a solution of either $Co(NH_3)_6Cl_3$, $Co(C_2H_{10}N_2)_3Cl_3$ or $[C_{18}H_{30}N_3]Br_3$ was followed by an immediate precipitation. The solid was washed with cold water and dried in vacuum. All three salts were synthesized according to the published methods [26–28]. The $[Mo_3S_7(Hmsa)_3]^{2-}$ unit crystallizes in a 1:1:1 ratio with the cation and one halogenid anion.

Anal. Calc. for $[Mo_3S_7(Hmsa)_3][Co(NH_3)_6]Cl\cdot H_2O$: C, 12.31; H, 2.75; N, 7.18; Mo, 24.57. Found: C, 12.58; H, 2.9; N, 6.75; Mo, 24.6%.

Calc. for $[Mo_3S_7(Hmsa)_3][Co(C_2H_{10}N_2)_3]Cl\cdot 2H_2O$: C, 17.06; H, 3.18; N, 6.63; Mo, 22.71. Found: C, 16.94; H, 3.17; N, 6.79; Mo, 22.74%.

Calc. for $[Mo_3S_7(Hmsa)_3][C_{18}H_{30}N_3]Br\cdot\frac{3}{2}H_2O$: C, 26.65; H, 3.35; N, 3.11; Mo, 21.29. Found: C, 26.55; H, 3.44; N, 3.35; Mo, 21.57%.

The analytical data indicate that the mba complex precipitates in a 3:2 ratio with the corresponding cations.

Anal. Calc. for $[Mo_3S_7(mba)_3]_3[Co(NH_3)_6]_2\cdot 6H_2O$: C, 22.68; H, 2.54; Mo, 25.88. Found: C, 22.92; H, 2.26; Mo, 25.37%.

Calc. for $[Mo_3S_7(mba)_3]_3[Co(C_2H_{10}N_2)_3]_2\cdot 9H_2O$: C, 25.40; H, 2.9; N, 4.74; Mo, 24.34. Found: C, 25.05; H, 2.68; N, 4.72; Mo, 24.37%.

Calc. for $[Mo_3S_7(mba)_3]_3[C_{18}H_{30}N_3]_2\cdot 9H_2O$: C, 32.62; H, 3.15; N, 2.31; Mo, 23.69. Found: C, 32.08; H, 2.89; N, 2.50; Mo, 23.67%.

Determination of pK Values

$[Mo_3S_7(Hmsa)_3]^{2-}$: 50 ml of a solution of 3 containing 0.741 mmol Mo in 1 M KCl were adjusted to 25 °C and kept under nitrogen. Base (0.2 M KOH, 0.8 M KCl) was added in increments of 0.1 ml. After the addition of 3.705 ml, a pH jump could be detected, indicating a Mo/H ratio of 1:1. Points between [OH]:[Mo] of 0.1 to 0.9 were used to calculate three p*K* values according to the method of minimization of the weighted residuals of the mass balance equations [29]. An ORION ROSS 8102SC combination pH electrode was used, which was calibrated before and after two determinations of the p*K*s by titration of 0.005 M HCl in 1 M KCl.

Mercapto-succinic acid (H_3msa): 50 ml of a solution of 0.01 M H_3msa in 1 M KCl was titrated with 0.2 M KOH in 0.8 M KCl as described for 3.

Physical Measurements

UV–Vis spectra were taken on a UVIKON 810, the ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker WM 250. The magnetic susceptibility was determined on a magnetic susceptibility balance (Johnson Matthey) at room temperature.

Collection of X-ray Data

An orange crystal of approximate dimension of 0.15 × 0.5 × 0.63 mm was sealed in a 0.5 mm ϕ glass capillary, including its mother liquor. The crystal was found to be of good quality by examination of rotation and Weissenberg photographs, and was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo Kα radiation. Crystal data are given in Table 1. Cell dimensions were determined by least-squares refinement of θ values of 25 reflections in the interval $9 < \theta < 22°$. Intensities of 8870 reflections (including standards) in the θ range 1–30° were collected using the ω–2θ scan technique, zigzag mode and variable scan speeds between 2.8 and 5.5° min^{-1}. The index range was $0 \leqslant h \leqslant 30$, $0 \leqslant k \leqslant 18$, $-26 \leqslant l \leqslant 26$. Four standard reflections were measured every 3 h during data collection and no loss of intensities was observed. Orientation was controlled using three standard reflections on an interval of every 400 reflections. 2457 of all measured reflections had negative intensities and were excluded from the data set. Of 6064 unique reflections 2952 were considered observed with $I \geqslant 3\sigma(I)$, 3112 were unobserved. The data were corrected for Lorentz and polarization effects and a numerical absorption correction was applied, min. and max. transmission factors are 0.514 and 0.828.

TABLE 1. Crystal data for $[C_{18}H_{30}N_3]_2[Mo_3S_7(Hmsa)_3]$-$[Mo_3S_7(Hmsa)_2(msa)]Br \cdot 6H_2O$ (Hmsa = $C_4H_4O_4S$, msa = $C_4H_3O_4S$)

Chemical formula	$C_{60}H_{95}N_6O_{30}S_{20}BrMo_6$
a (Å)	21.968(7)
b (Å)	13.423(13)
c (Å)	18.828(3)
β (°)	94.23(2)
V (Å^3)	5537(8)
Z	2
Space group	C2 (No. 5 International Tables)
μ(Mo Kα) (cm^{-1})	13.51
M_r	2677.256
D_c (g cm^{-3})	1.606
F(000)	2688
R	0.0799
R_w	0.0935
No. measured reflections	8870
No. observed reflections	2952

Solution of the Structure and Refinement

Systematic absences of reflections hkl with $h + k = 2n + 1$ led to possible space group $C2/m$, $C2$ or Cm. The structure was solved by the Patterson method using SHELXS86 [30] in the space group $C2$. Comparison of $C2/m$ and $C2$ refinements by using the Hamilton test [31] unambiguously favoured the space group $C2$. The structure was refined with SHELX76 [32]. The carbonyl groups of the mercapto-succinic acid and the atomic position of the hexamethyl-tripyrrolium cation were localized later after several refinement cycles in the difference Fourier map. However, distances and angles of C(1), C(2) and the outer part of msa (C(3), C(4), O(3), O(4)) and of the tripyrrolium moiety were not in good agreement with the expected or observed values [28]. Therefore all these organic parts of the structure except the sulfur atoms were treated as fixed models during the refinement. In addition, it was not possible to distinguish the protonated form ($-CH_2-COOH$) from the deprotonated form ($-CH_2-COO^-$) of the anion. Finally, three water positions could be found and three hydrogen atomic positions were localized for the Hmsa molecule. In the final full matrix refinement cycles, the positional and anisotropic temperature parameters of the Mo, Br and S atoms and of the coordinating part of the msa molecules (S(6), O(1), O(2), C(1), C(2)) were varied. The C and N atoms of the tripyrrolium cation were varied as fixed models with anisotropic temperature parameters. The positions of the 30 hydrogen atoms of the cation were calculated and included in the refinement with fixed C–H distances of 1.08 Å and fixed isotropic temperature parameters. The refinement was stopped at $R = 7.99\%$ ($R_w = 9.35$, $w = 1$) with a maximum shift to e.s.d. ratio of 0.25. The maximum and minimum heights in the final difference Fourier synthesis were 1.21 e Å^{-3} (1.33 Å from Mo(1)) and −1.27 e Å^3. Calculations were performed on a Hitachi ASXL 60 computer. Atomic scattering factors were those of SHELX and of the International Tables for X-ray Crystallography [33]. The final atomic parameters are listed in Table 2, selected bond lengths and angles are given in Tables 3 and 4.

Results and Discussion

Preparation of $[Mo_3S_7]^{4+}$ Complexes

It seems that direct ligand exchange on the $[Mo_3S_7]^{4+}$ core has never been used for the synthesis of new derivatives. Instead of simple ligand exchange on treating $[Mo_3S_7]^{4+}$ complexes with possible ligands, the already mentioned conversion to $[Mo_3S_4]^{4+}$ derivatives has been observed [3, 4]. For instance, the treatment of $[Mo_3S_7(S_2)_3]^{2-}$ with nitrilotriacetic acid and oxalic acid leads to $\{Mo_3S_4$-

TABLE 2. Positional and isotropic or equivalent isotropic thermal parameters with e.s.d.s in parentheses

Atom	x	y	z	U_{eq} (Å^2)[a]
Mo(1)	0.1588(3)	0.1078(16)	0.1609(3)	0.0554(12)
Mo(2)	0.1591(2)	−0.0967(16)	0.1613(3)	0.0490(12)
Mo(3)	0.2049(1)	0.0061(17)	0.0504(1)	0.0603(8)
Br(1)	0.0000	0.0033(20)	0.0000	0.0743(12)
S(1)	0.1210(4)	0.0041(23)	0.2586(4)	0.0626(18)
S(2)	0.0691(3)	0.0045(21)	0.1648(4)	0.0604(17)
S(3A)	0.2059(8)	0.1899(23)	0.0609(10)	0.0971(37)
S(3B)	0.2061(6)	−0.1832(19)	0.0601(9)	0.0537(25)
S(4A)	0.1226(8)	0.1273(23)	0.0375(9)	0.0863(34)
C(1A)	0.1155(16)	0.3034(31)	0.2244(22)	0.133(5)
C(2A)	0.1662(18)	0.2885(42)	0.2801(17)	0.086(5)
O(1A)	0.1033(14)	0.2260(30)	0.1830(18)	0.060(4)
O(2A)	0.0714(16)	0.3482(33)	0.2448(22)	0.103(4)
C(2B)	0.1741(15)	−0.2862(45)	0.2600(26)	0.126(5)
O(1B)	0.0972(22)	−0.2198(29)	0.1784(18)	0.084(5)
O(2B)	0.0786(28)	−0.3554(37)	0.2341(33)	0.204(4)
C(1C)	0.2491(9)	0.0157(47)	−0.1001(9)	0.081(4)
C(2C)	0.3105(10)	0.0269(42)	−0.0624(14)	0.126(5)
O(1C)	0.2008(8)	0.0180(41)	−0.0630(9)	0.081(4)
O(2C)	0.2411(10)	0.0237(36)	−0.1650(10)	0.093(4)
C(N11)	0.8490(13)	0.7248(32)	0.1365(25)	0.066(4)
C(N12)	0.9547(25)	0.8072(35)	0.1492(27)	0.099(4)
N(1)	0.9146(12)	0.7203(30)	0.1693(17)	0.110(5)
C(7A)	0.9068(18)	0.7106(28)	0.2488(18)	0.073(5)
C(8A)	0.9399(22)	0.6171(29)	0.1544(25)	0.086(5)
C(1)	0.8938(25)	0.6018(27)	0.2557(17)	0.078(4)
C(2)	0.9173(17)	0.5415(24)	0.2045(18)	0.051(4)
C(3)	0.9145(19)	0.4383(24)	0.2070(17)	0.066(4)
C(4)	0.8936(18)	0.3949(27)	0.2674(16)	0.057(4)
C(5)	0.8719(30)	0.4584(30)	0.3180(22)	0.101(4)
C(6)	0.8709(20)	0.5618(30)	0.3163(18)	0.048(4)
C(N21)	0.8457(17)	0.2530(35)	0.1317(24)	0.068(4)
C(N22)	0.9459(30)	0.1824(38)	0.1662(31)	0.124(5)
N(2)	0.9066(16)	0.2752(33)	0.1727(18)	0.112(4)
C(7B)	0.8950(25)	0.2859(28)	0.2512(20)	0.083(4)
C(8B)	0.9398(28)	0.3702(31)	0.1536(29)	0.109(5)
C(7C)	0.8394(23)	0.5948(28)	0.3800(21)	0.085(5)
C(8C)	0.8557(19)	0.4062(31)	0.3841(19)	0.065(4)
C(N31)	0.7560(13)	0.5099(71)	0.3895(22)	0.125(4)
C(N32)	0.8268(24)	0.5210(53)	0.4928(13)	0.147(5)
N(3)	0.8232(12)	0.4959(29)	0.4136(11)	0.092(4)
Atom	x	y	z	U_{iso} (Å^2)
C(3A)	0.1481(18)	0.2740(48)	0.3571(17)	0.15(1)
C(4A)	0.2062(15)	0.2677(32)	0.4025(18)	0.39(1)
O(3A)	0.1892(19)	0.2326(36)	0.4632(18)	0.18(1)
O(4A)	0.2462(19)	0.3310(42)	0.4020(28)	0.22(1)
C(1B)	0.1089(13)	−0.2788(27)	0.2334(16)	0.047(7)
C(3B)	0.1932(17)	−0.3560(34)	0.3229(18)	0.105(9)
C(4B)	0.2483(14)	−0.3216(29)	0.3666(16)	0.23(1)
O(3B)	0.2259(18)	−0.2809(33)	0.4226(19)	0.147(9)
O(4B)	0.2957(15)	−0.3698(41)	0.3730(24)	0.22(1)
C(3C)	0.3594(11)	−0.0348(28)	−0.0974(18)	0.079(8)
C(4C)	0.4250(10)	−0.0311(24)	−0.0721(12)	0.15(1)
O(3C)	0.4340(14)	−0.1158(26)	−0.0377(21)	0.156(9)
O(4C)	0.4498(15)	0.0449(27)	−0.0483(21)	0.19(1)
O(W1)	0.5486(13)	0.0054(67)	0.3380(16)	0.137(8)
O(W2)	0.9536(29)	0.0231(82)	0.3003(35)	0.36(1)
O(W3)	0.3220(34)	0.4568(59)	0.2775(39)	0.36(1)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j \mathbf{a}_i \mathbf{a}_j$.

TABLE 3. Bond distances (Å) with their e.s.d.s in parentheses

Mo(1)---Mo(2)	2.745(4)	N(1)---C(N11)	1.525(5)
Mo(1)-- Mo(3)	2.744(8)	N(1)---C(N12)	1.526(5)
Mo(2)---Mo(3)	2.753(6)	N(1)---C(7A)	1.526(5)
Mo(1)---S(1)	2.498(15)	N(1)---C(8A)	1.526(5)
Mo(1)---S(2)	2.416(11)	N(2)---C(N22)	1.525(5)
Mo(1)---S(3A)	2.473(19)	N(2)---C(N21)	1.525(5)
Mo(1)---S(4A)	2.414(19)	N(2)---C(7B)	1.525(5)
Mo(1)---S(5)	2.391(14)	N(2)---C(8B)	1.525(5)
Mo(1)---S(6A)	2.437(14)	N(3)---C(7C)	1.525(5)
Mo(1)---O(1A)	2.061(32)	N(3)---C(8C)	1.525(5)
Mo(2)---S(1)	2.473(14)	N(3)---C(N31)	1.524(5)
Mo(2)---S(2)	2.404(16)	N(3)---C(N32)	1.525(5)
Mo(2)---S(3B)	2.517(16)	C(1)---C(2)	1.388(5)
Mo(2)---S(4B)	2.415(15)	C(1)---C(7A)	1.495(5)
Mo(2)---S(5)	2.329(16)	C(1)---C(6)	1.388(5)
Mo(2)---S(6B)	2.438(20)	C(2)---C(8A)	1.495(5)
Mo(2)---O(1B)	2.179(39)	C(2)---C(3)	1.388(5)
Mo(3)---S(3A)	2.475(26)	C(3)---C(4)	1.388(5)
Mo(3)---S(3B)	2.547(17)	C(3)---C(8B)	1.495(5)
Mo(3)---S(4A)	2.431(21)	C(4)---C(5)	1.388(5)
Mo(3)---S(4B)	2.448(14)	C(4)---C(7B)	1.495(5)
Mo(3)---S(5)	2.353(7)	C(5)---C(6)	1.388(5)
Mo(3)---S(6C)	2.422(8)	C(5)---C(8C)	1.495(5)
Mo(3)---O(1C)	2.137(17)	C(6)---C(7C)	1.495(5)
S(1)---S(2)	2.032(10)		
S(4A)---S(3A)	2.031(28)		
S(4B)---S(3B)	2.049(17)		
C(1A)---C(2A)	1.485(5)		
C(1A)---O(1A)	1.315(5)		
C(1A)---O(2A)	1.225(5)		
C(2A)---S(6A)	1.823(46)		
C(2A)---C(3A)	1.545(5)		
C(3A)---C(4A)	1.485(5)		
C(4A)---O(3A)	1.314(5)		
C(4A)---O(4A)	1.225(5)		
C(1B)---C(2B)	1.485(5)		
C(1B)---O(1B)	1.315(5)		
C(1B)---O(2B)	1.225(5)		
C(2B)---S(6B)	1.713(50)		
C(2B)---C(3B)	1.543(5)		
C(3B)---C(4B)	1.485(5)		
C(4B)---O(3B)	1.315(5)		
C(4B)---O(4B)	1.224(5)		
C(1C)---C(2C)	1.484(5)		
C(1C)---O(1C)	1.314(5)		
C(1C)---O(2C)	1.225(5)		
C(2C)---S(6C)	1.775(30)		
C(2C)---C(3C)	1.544(5)		
C(3C)---C(4C)	1.485(5)		
C(4C)---O(3C)	1.316(5)		
C(4C)---O(4C)	1.225(5)		

TABLE 4. Bond angles (°) with e.s.d.s. in parentheses

Mo(2)–Mo(1)–Mo(3)	60.2(2)
S(1)–Mo(1)–Mo(2)	56.0(5)
S(1)–Mo(1)–Mo(3)	116.2(5)
S(1)–Mo(1)–S(2)	48.8(3)
S(2)–Mo(1)–Mo(2)	55.1(5)
S(2)–Mo(1)–Mo(3)	94.9(4)
S(3a)–Mo(1)–Mo(2)	116.5(7)
S(3a)–Mo(1)–Mo(3)	56.4(6)
S(3a)–Mo(1)–S(1)	171.7(7)
S(2a)–Mo(1)–S(2)	131.8(6)
S(4a)–Mo(1)–Mo(2)	96.4(6)
S(4a)–Mo(1)–Mo(3)	55.8(5)
S(4a)–Mo(1)–S(1)	131.8(6)
S(4a)–Mo(1)–S(2)	83.1(5)
S(4a)–Mo(1)–S(3a)	49.1(6)
S(5)–Mo(1)–Mo(2)	53.4(5)
S(5)–Mo(1)–Mo(3)	54.0(2)
S(5)–Mo(1)–S(1)	86.0(5)
S(5)–Mo(1)–S(2)	108.2(6)
S(5)–Mo(1)–S(3a)	86.2(6)
S(5)–Mo(1)–S(4a)	109.5(5)
S(6a)–Mo(1)–Mo(2)	122.3(5)
S(6a)–Mo(1)–Mo(3)	122.5(5)
S(6a)–Mo(1)–S(1)	91.3(6)
S(6a)–Mo(1)–S(2)	136.3(6)
S(6a)–Mo(1)–S(3a)	90.4(7)
S(6a)–Mo(1)–S(4a)	135.1(7)
S(6a)–Mo(1)–S(5)	81.5(6)
O(1a)–Mo(1)–Mo(2)	140.4(11)
O(1a)–Mo(1)–Mo(3)	142.5(10)
O(1a)–Mo(1)–S(1)	92.7(12)
O(1a)–Mo(1)–S(2)	86.5(11)
O(1a)–Mo(1)–S(3a)	95.6(13)
O(1a)–Mo(1)–S(4a)	87.4(10)
O(1a)–Mo(1)–S(5)	158.4(9)
O(1a)–Mo(1)–S(6a)	77.0(9)
Mo(1)–Mo(2)–Mo(3)	59.9(3)
S(1)–Mo(2)–Mo(1)	56.9(5)
S(1)–Mo(2)–Mo(3)	116.8(5)
S(2)–Mo(2)–Mo(1)	55.5(4)
S(2)–Mo(2)–Mo(3)	94.9(3)
S(2)–Mo(2)–S(1)	49.2(3)
S(3b)–Mo(2)–Mo(1)	117.4(5)
S(3b)–Mo(2)–Mo(3)	57.6(4)
S(3b)–Mo(2)–S(1)	173.5(6)
S(3b)–Mo(2)–S(2)	131.7(4)
S(4b)–Mo(2)–Mo(1)	96.4(5)
S(4b)–Mo(2)–Mo(3)	56.1(4)
S(4b)–Mo(2)–S(1)	132.0(5)
S(4b)–Mo(2)–S(2)	82.9(4)
S(4b)–Mo(2)–S(3b)	49.0(4)
S(5)–Mo(2)–Mo(1)	55.5(5)
S(5)–Mo(2)–Mo(3)	54.4(2)
S(5)–Mo(2)–S(1)	88.0(5)
S(5)–Mo(2)–S(2)	110.7(6)
S(5)–Mo(2)–S(3b)	85.9(5)
S(5)–Mo(2)–S(4b)	109.8(4)
S(6b)–Mo(2)–Mo(1)	120.8(5)
S(6b)–Mo(2)–Mo(3)	123.1(4)
S(6b)–Mo(2)–S(1)	89.0(6)
S(6b)–Mo(2)–S(2)	134.7(5)
S(6b)–Mo(2)–S(3b)	91.9(5)
S(6b)–Mo(2)–S(4b)	137.0(6)
S(6b)–Mo(2)–S(5)	79.2(6)
O(1b)–Mo(2)–Mo(1)	139.2(12)
O(1b)–Mo(2)–Mo(3)	139.4(10)
O(1b)–Mo(2)–S(1)	93.2(12)
O(1b)–Mo(2)–S(2)	84.3(12)
O(1b)–Mo(2)–S(3b)	93.3(12)
O(1b)–Mo(2)–S(4b)	83.7(10)
O(1b)–Mo(2)–S(5)	160.5(10)
O(1b)–Mo(2)–S(6b)	81.3(10)
Mo(1)–Mo(3)–Mo(2)	59.9(1)
S(3a)–Mo(3)–Mo(1)	56.3(5)
S(3a)–Mo(3)–Mo(2)	116.1(5)
S(3b)–Mo(3)–Mo(1)	116.4(4)
S(3b)–Mo(3)–Mo(2)	56.5(4)
S(3b)–Mo(3)–S(3a)	171.4(3)
S(4a)–Mo(3)–Mo(1)	55.2(5)
S(4a)–Mo(3)–Mo(2)	95.8(4)
S(4a)–Mo(3)–S(3a)	48.9(7)
S(4a)–Mo(3)–S(3b)	132.7(6)
S(4b)–Mo(3)–Mo(1)	95.6(4)
S(4b)–Mo(3)–Mo(2)	54.9(4)
S(4b)–Mo(3)–S(3a)	133.1(6)
S(4b)–Mo(3)–S(3b)	48.4(5)
S(4b)–Mo(3)–S(4a)	84.6(3)
S(5)–Mo(3)–Mo(1)	55.3(4)
S(5)–Mo(3)–Mo(2)	53.6(4)
S(5)–Mo(3)–S(3a)	87.0(7)
S(5)–Mo(3)–S(3b)	84.7(7)
S(5)–Mo(3)–S(4a)	110.2(6)
S(5)–Mo(3)–S(4b)	107.9(6)
S(6c)–Mo(3)–Mo(1)	121.7(6)
S(6c)–Mo(3)–Mo(2)	122.5(6)
S(6c)–Mo(3)–S(3a)	89.7(10)
S(6c)–Mo(3)–S(3b)	91.2(10)
S(6c)–Mo(3)–S(4a)	134.7(10)
S(6c)–Mo(3)–S(4b)	135.9(10)
S(6c)–Mo(3)–S(5)	80.0(3)
O(1c)–Mo(3)–Mo(1)	136.8(13)
O(1c)–Mo(3)–Mo(2)	143.5(11)
O(1c)–Mo(3)–S(3a)	90.3(15)
O(1c)–Mo(3)–S(3b)	98.4(15)
O(1c)–Mo(3)–S(4a)	82.7(11)
O(1c)–Mo(3)–S(4b)	88.7(11)
O(1c)–Mo(3)–S(5)	159.4(6)
O(1c)–Mo(3)–S(6c)	79.6(5)
Mo(1)–S(1)–Mo(2)	67.0(2)
S(2)–S(1)–Mo(1)	63.5(5)
S(2)–S(1)–Mo(2)	63.6(5)
Mo(1)–S(2)–Mo(2)	69.4(2)
S(1)–S(2)–Mo(1)	67.7(5)
S(1)–S(2)–Mo(2)	67.1(6)
Mo(1)–S(3a)–Mo(3)	67.4(6)
S(4a)–S(3a)–Mo(1)	63.9(7)
S(4a)–S(3a)–Mo(3)	64.4(9)
Mo(2)–S(3b)–Mo(3)	65.9(4)

(continued)

TABLE 4. *(continued)*

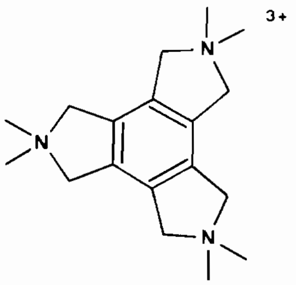
S(4b)–S(3b)–Mo(2)	62.9(6)
S(4b)–S(3b)–Mo(3)	63.3(5)
Mo(1)–S(4a)–Mo(3)	69.0(5)
S(3a)–S(4a)–Mo(1)	67.0(8)
S(3a)–S(4a)–Mo(3)	66.7(9)
Mo(2)–S(4b)–Mo(3)	69.0(3)
S(3b)–S(4b)–Mo(2)	68.1(6)
S(3b)–S(4b)–Mo(3)	68.3(6)
Mo(1)–S(5)–Mo(2)	71.1(2)
Mo(1)–S(5)–Mo(3)	70.7(3)
Mo(2)–S(5)–Mo(3)	72.0(4)

$[N(CH_2CO_2)_3]_3(H)_2\}^{3-}$ [15] and $[Mo_3S_4(C_2O_4)_3(H_2O)_3]^{2-}$ [6]. We found that $[Mo_3S_7(S_2)_3]^{2-}$ can be converted in reasonable yield in chloroform and concentrated hydrobromic acid to $[Mo_3S_7Br_6]^{2-}$, which can be isolated as the tetraethylammonium salt. It is noteworthy that the Mo_3S_7 core remains unchanged under these rigorous conditions. Using an excess of mercapto-succinic acid (H_3msa) and triethylamine as base, the six Br^- ligands are removed and $[Mo_3S_7(Hmsa)_3]^{2-}$ is formed. To confirm that $[Mo_3S_7Br_6]^{2-}$ serves as a suitable intermediate for the synthesis of Mo_3S_7 complexes, we also treated $[Mo_3S_7Br_6]^{2-}$ with 2-mercapto-benzoic acid (H_2mba). Analysis and spectroscopic data of the product are in agreement with the formation of $[Mo_3S_7(mba)_3]^{2-}$.

$$\begin{tikzcd}
 & & {[Mo_3S_7(Hmsa)_3]^{2-}} \\
{[Mo_3S_7(S_2)_3]^{2-}} \arrow[r, "HBr"] & {[Mo_3S_7Br_6]^{2-}} \arrow[ur, "H_3msa"] \arrow[dr, "H_2mba"'] & \\
 & & {[Mo_3S_7(mba)_3]^{2-}}
\end{tikzcd}$$

Characterization of $[Mo_3S_7(Hmsa)_3]^{2-}$ and $[Mo_3S_7(mba)_3]^{2-}$

Both complexes were first isolated as a mixture of tetraethyl- and triethylammonium salts. As already known for other Mo_3S_7 complexes, they are diamagnetic. The mba complex is slightly and the msa complex is moderately soluble in water, whereas both are soluble in dimethylformamide and dimethyl sulfoxide. It is, however, rather difficult to obtain crystalline solids of defined composition. Cotton *et al.* reported similar difficulties in isolating complexes of $[Mo_3S_4]^{4+}$ with nitrilotriacetate or oxalate [15]. Our complexes can be precipitated almost quantitatively from hot and cold aqueous solutions by the addition of the large cations (charged 3+) hexaammincobalt(III) $Co(NH_3)_6^{3+}$, tris-ethylenediamincobalt(III) $Co(H_2NCH_2CH_2NH_2)_3^{3+}$ and octahydro-hexamethyl-benzotripyrrolium (ohb).



Yellow or orange crystals of well defined composition were obtained this way. With ohb, two distinct forms of crystals were observed. When the cation was dissolved in 1 M KBr and the $[Mo_3S_7(Hmsa)_3]^{2-}$ complex was dissolved in water separately, slow diffusion of the two solutions gave long needles (up to 1 mm) which were stable in air, but the diameter was too small for X-ray diffraction (less than 0.01 mm). Analysis fits best for $[C_{18}H_{30}N_3][Mo_3S_7(Hmsa)_3]Br\cdot\frac{3}{2}H_2O$. Slow evaporation of a saturated solution of the above mentioned precipitate gave monoclinic platelets which decayed immediately after removal of its mother liquor due to the loss of water. As long as they were kept in the solvent they were absolutely stable so that a single X-ray crystal structure analysis could be performed after transfer into a glass capillary. The composition is $[C_{18}H_{30}N_3]_2[Mo_3S_7(Hmsa)_3][Mo_3S_7(Hmsa)_2(msa)]Br\cdot 6H_2O$. We suggest, that ohb is a particularly suitable agent for the precipitation and crystallization of negatively charged Mo_3S_4 and Mo_3S_7 complexes.

Aqueous solutions of $[Mo_3S_7(Hmsa)_3]^{2-}$ are acidic and by addition of base, three protons can be removed reversibly, finally forming $[Mo_3S_7(msa)_3]^{5-}$. From the neutralization curve (Fig. 1) the p*K* values 3.95, 4.41, 5.02 (1 M KCl, 25 °C) were

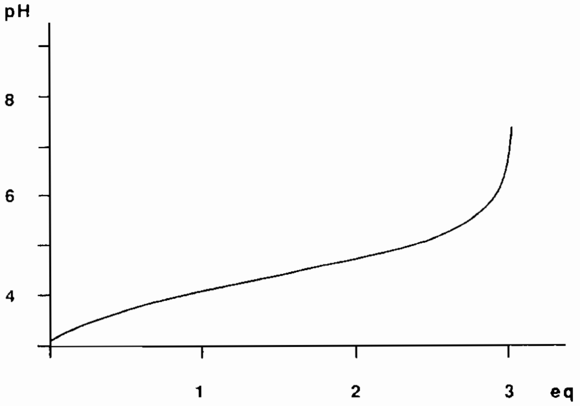


Fig. 1. Neutralization of $[Mo_3S_7(Hmsa)_3]^{2-}$ in 1 M KCl with KOH (25 °C). eq = mol KOH/mol $[Mo_3S_7(Hmsa)_3]$.

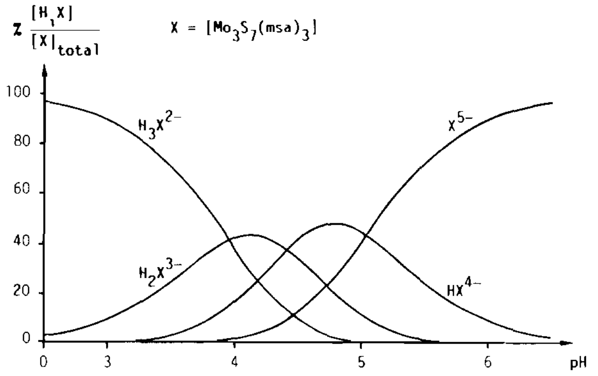


Fig. 2. Equilibrium distribution of species $H_i[Mo_3S_7(msa)_3]$.

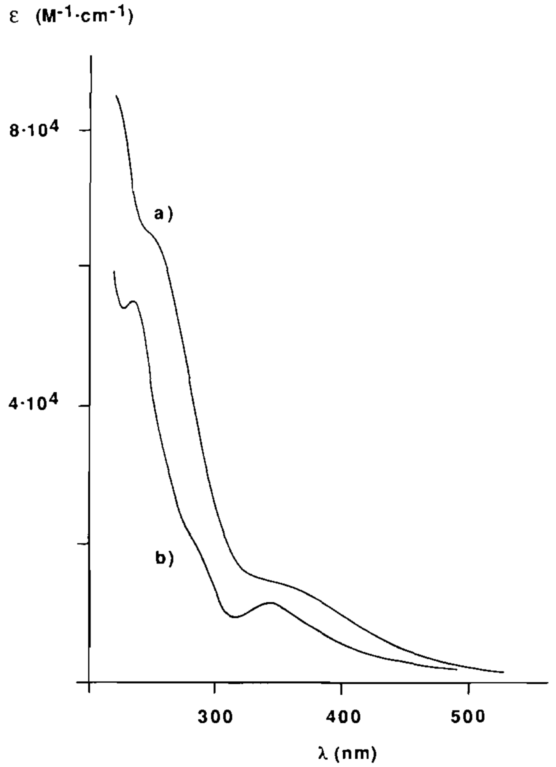


Fig. 3. UV–Vis spectra of: (a) $[Mo_3S_7(mba)_3]^{2-}$, (b) $[Mo_3S_7(Hmsa)_3]^{2-}$ in H_2O.

calculated. This obviously allows the total charge to be altered from −2 to −5 as demonstrated in Fig. 2. The pK values of the free H_3msa in 1 M KCl were found to be 3.03, 4.40, 9.92 (SH). Over the pH range of 1 to 12 no symptoms of decomposition of the complex could be observed.

Spectroscopic Properties

The UV–Vis spectra of $[Mo_3S_7(Hmsa)_3]^{2-}$ and $[Mo_3S_7(mba)_3]^{2-}$ are shown in Fig. 3. Both complexes show similar spectra. It is remarkable that there is no maximum below 400 nm. This seems to be in disagreement with an earlier discussion of electronic transitions of $[Mo_3S_7]^{4+}$ complexes [34]. The ^{1}H NMR spectrum confirms the stability of the $[Mo_3S_7(Hmsa)_3]^{2-}$ unit in water. The spectrum was measured in D_2O: three protons of msa could be observed at 3.65 ppm (1 H) and 2.66 ppm (2 H). The pattern and the chemical shifts are quite different from free msa, which could never be detected in the solution of the complex.

Molecular Structure of $[Mo_3S_7(Hmbs)_3]^{2-}$

The ligand msa^{3-} has three possible binding sites (S$^-$, two COO$^-$). It is, however, very unlikely that all the three are bound to the Mo_3S_7 core. The three pK values of $[Mo_3S_7(Hmsa)_3]^{2-}$ rather indicate that one of the carboxylic groups can be reversibly deprotonated and therefore is not involved in binding. For Mo_3S_4 complexes, it has been reported that bidentate ligands can either bind to one single or bridge to two different Mo atoms [12]. Due to the more bulky disulfido groups in Mo_3S_7 compared to the monosulfido groups in Mo_3S_4 bridging seems rather unlikely. Thus, considering bidentate coordination of msa with S$^-$ and COO$^-$ bound to the same Mo atom, there is still a large variety of possible isomers which must be taken into account:

- Depending on which of the two carboxylic groups is coordinated, a five- or six-membered ring will be formed.
- Focussing the μ_3-S atom which caps the Mo_3 triangle the S atom of msa can either be located on the same (*cis*) or on the opposite side (*trans*) of the triangle. Therefore, the four different stereoisomers can be labelled all-*cis*/*cis,cis,trans*/*cis,trans,trans*/ or all-*trans*.
- Moreover the chirality of msa causes additional possibilities for isomerism. For each of the forms mentioned above, two diastereomeric pairs of enantiomers (*R,R,R*), (*S,S,S*) and (*R,R,S*), (*S,S,R*) must be considered.

According to the X-ray structure analysis, the coordinated msa molecules form a five-membered ring (Figs. 4 and 5) and the all-*cis* form was observed. The refinement in the space group *C*2 exhibited that only one of the four diastereomeric forms was present, which was either (*R,R,S*) or (*S,S,R*). The structural features of the Mo_3S_7 core itself was very similar to those reported previously for other Mo_3S_7 compounds [18, 22, 23, 25]. The planes defined by the S, O and Mo atoms of the five-membered rings are oriented approximately perpendicular to the Mo_3 triangle, which can be seen in Fig. 5. The corresponding angles are 89.3° (a), 91.7° (b) and 87.9° (c). A stereoview of the entire unit cell is presented in Fig. 6.

It should be noted that only a small amount of the complex was obtained as single crystals from aqueous solution and that other isomers could well be formed and remain in solution. The ^{13}C NMR spectrum in

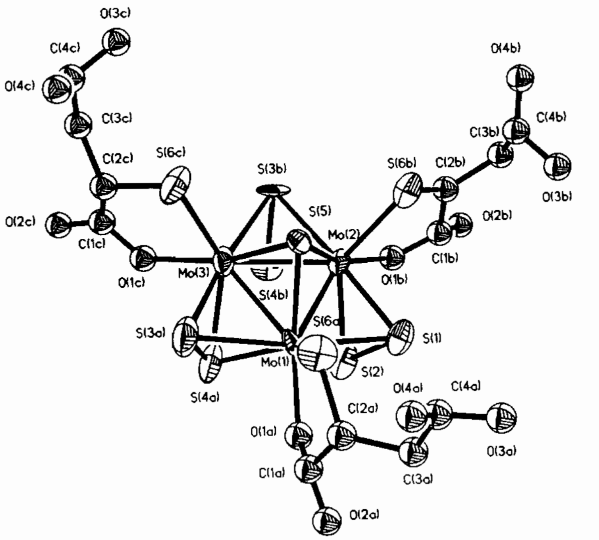


Fig. 4. Structure of $[Mo_3S_7(Hmsa)_3]^{2-}$ ORTEP [35] drawing with numbering scheme and vibrational ellipsoids at the 50% probability level, isotropically refined atoms of the msa entities are shown as spheres of arbitrary size.

D_2O, however, shows only four signals for the coordinated msa molecules (188.0, 178.4, 45.1, 43.5 ppm). This result clearly limits the variety of the isomers formed.

Supplementary Material

Additional data to this paper can be ordered referring to the no. CSD 53888, names of the authors and citation of the paper at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D 7514 Eggenstein-Leopoldshafen 2.

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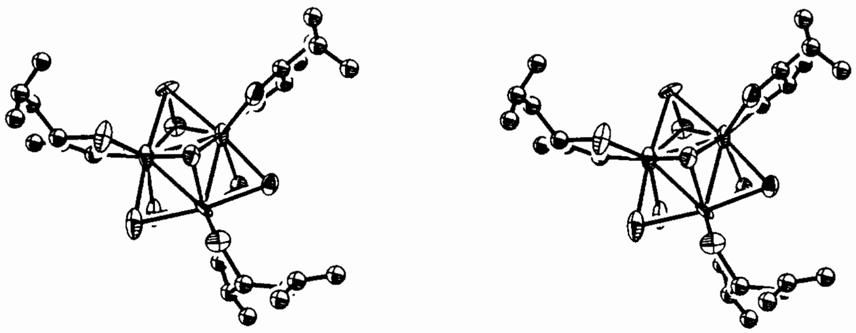

Fig. 5. Stereoview of $[Mo_3S_7(Hmsa)_3]^{2-}$; ORTEP [35] plot with vibrational ellipsoids at the 50% probability level.

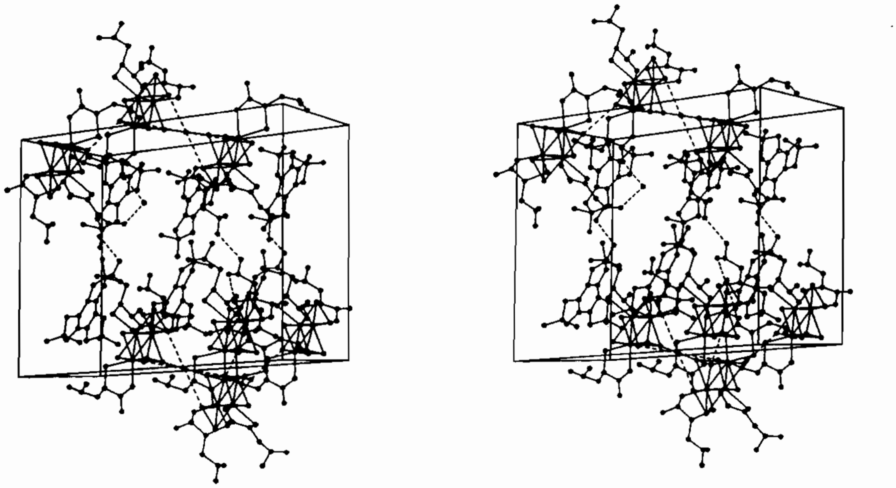

Fig. 6. Stereoview of the unit cell of $[C_{18}H_{30}N_3]_2[Mo_3S_7(Hmsa)_3][Mo_3S_7(Hmsa)_2msa]Br \cdot 6H_2O$. Possible intermolecular hydrogen bonds and sulfur bromine contacts are indicated by broken lines.

References

1 F. A. Cotton, *Polyhedron, 5* (1986) 3.
2 A. Müller, *Polyhedron, 5* (1986) 323.
3 A. Müller and U. Reinsch, *Angew. Chem., 92* (1980) 69.
4 H. Keck, W. Kuchen, J. Mathow and H. Wunderlich, *Angew. Chem., 94* (1982) 927.
5 T. R. Halbert, K. McGauley, W.-H. Pan, R. S. Czernuszewicz and E. I. Stiefel, *J. Am. Chem. Soc., 106* (1984) 1849.
6 F. A. Cotton, Z. Dori, R. Llusar and W. Schwotzer, *J. Am. Chem. Soc., 107* (1985) 6734.
7 P. Kathirgamanathan, M. Martinez and G. Sykes, *Polyhedron, 5* (1986) 505.
8 A. Müller, R. Jostes, W. Eltzner, Chong-Shi Nie, E. Diemann, H. Bögge, M. Zimmermann, M. Dartmann, U. Reinsch-Vogell, Shun Che, S. J. Cyvin and B. N. Cyvin, *Inorg. Chem., 24* (1985) 2872.
9 F. A. Cotton and R. Llusar, *Polyhedron, 6* (1987) 1741.
10 T. Saito, N. Yamamoto, T. Yamagata and H. Imoto, *Chem. Lett.,* (1987) 2025.
11 P. J. Vergamini, H. Vahrenkamp and L. F. Dahl, *J. Am. Chem. Soc., 93* (1971) 6327.
12 H. Wunderlich, *Acta Crystallogr., Sect. C, 43* (1987) 24.
13 J. Q. Huang, J. L. Huang, M. Y. Shang, S. F. Lu, X. T. Lin, Y. H. Lin, M. D. Huang, H. H. Zhuang and J. X. Lu, *Pure Appl. Chem., 60* (1988) 1185.
14 T. Shibahara and H. Kuroya, *Polyhedron, 5* (1986) 357.
15 F. A. Cotton, R. Llusar, D. O. Marler, W. Schwotzer and Z. Dori, *Inorg. Chim. Acta, 102* (1985) L25.
16 F. A. Cotton, Z. Dori, R. Llusar and W. Schwotzer, *Inorg. Chem., 25* (1986) 3654.
17 P. Kathirgamanathan, M. Martinez and G. Sykes, *Chem. Commun.,* (1985) 1437.
18 J. Marcoll, A. Rabenau, D. Mootz and H. Wunderlich, *Rev. Chim. Miner., 11* (1974) 607.
19 V. P. Fedin, S. P. Gubin, A. V. Mishchenko and V. E. Fedorov, *Koord. Khim., 10* (1984) 901.
20 P. Klingelhöfer, U. Müller, C. Friebel and J. Pebler, *Z. Anorg. Allg. Chem., 543* (1986) 22.
21 J. Huang, M. Shang and J. Lu, *Scientia Sinica (B), 26* (1983) 1121.
22 A. Müller, S. Pohl, M. Dartmann, J. P. Cohen, J. M. Bennett and R. M. Kirchner, *Z. Naturforsch., Teil B, 34* (1979) 434.
23 M. Shang, J. Huang and J. Lu, *Acta Crystallogr., Sect. C, 40* (1984) 759.
24 B. Meyer and H. Wunderlich, *Z. Naturforsch., Teil B, 37* (1982) 1437.
25 A. Müller, R. G. Bhattacharyya and B. Pfefferkorn, *Chem. Ber., 112* (1979) 778.
26 R. D. Lindholm and D. E. Bause, *Inorg. Synth., 18* (1978) 67.
27 J. B. Work and J. P. McReynolds, *Inorg. Synth., 2* (1946) 221.
28 J. Ciric, S. L. Lawton, G. T. Kokotailo and G. W. Griffin, *J. Am. Chem. Soc., 100* (1978) 2173.
29 G. Anderegg, *Helv. Chim. Acta, 44* (1961) 1673.
30 G. M. Sheldrick, SHELXS86, in G. M. Sheldrick, C. Krüger and R. Goddard (eds.), *Crystallographic Computing,* Oxford University Press, London, 1985, p. 175.
31 W. C. Hamilton, *Acta Crystallogr., 18* (1965) 502.
32 G. M. Sheldrick, *SHELX76,* program for crystal structure determination, University of Cambridge, U.K., 1976.
33 *International Tables for X-ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, 1974, p. 99.
34 A. Müller, R. Jostes, W. Jaegermann and R. G. Bhattacharyya, *Inorg. Chim. Acta, 41* (1980) 259.
35 C. K. Johnson, *ORTEP, Report ORNL-3794 (revised),* Oak Ridge National Laboratory, TN, 1971.