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Synthesis and Molecular Structure of $[Ni_4(S_2)(SCH_2CH_2S)_4]^{2-}$, a Mixed Nickel–Disulfide–Thiolate Anion with a Prismatic Ni_4S_2 Core

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The reaction system $NiCl_2/Na_2edt/S_2^{2-}$ (edt^{2-} = 1,2-ethanedithiolate) in a 4:4:1 ratio in methanol affords the $[Ni_4(S_2)(edt)_4]^{2-}$ anion (**1**), which was isolated as its Ph_4P^+ salt. $[Ph_4P]_2[Ni_4(S_2)(edt)_4]\cdot MeOH$ (**2**) crystallizes in the triclinic space group $P\bar{1}$ with a = 11.506 (6) Å, b = 11.902 (6) Å, c = 23.152 (13) Å, α = 104.10 (4)°, β = 97.23 (4)°, γ = 105.73 (4)°, and Z = 2. The structure was refined to R = 0.057. The metal sulfide framework of **1** has a mixed prismane type structure with four nickel atoms in a rectangular arrangement. Each nickel atom is coordinated to one terminal and one bridging sulfur atom of an edt^{2-} ligand, affording a distorted-square-planar NiS_4 unit in a structure that ideally has C_{2v} symmetry. **1** is a rare example of a complex simultaneously containing polysulfide and thiolate groups coordinated to one metal. This species and the recently reported anions $[Ni_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$ (**3**) and $[Ni_3S(SMe)_6]^{2-}$ (**4**) are the only structurally characterized $Ni\text{–}S_n\text{–}SR$ complexes ($n \geq 1$). Solution spectral and solid-state magnetic properties are indicative of square-planar NiS_4 chromophores similar to those present in $[Ni(S_4)_2]^{2-}$.

Introduction

Complexes with metal–sulfur coordination sites are of significant interest as possible synthetic models for the active sites of metalloproteins[1] and metal sulfide heterogeneous catalysts.[2] In both of these contexts it is desirable to find rational, high-yield synthetic routes to transition-metal–sulfur clusters. Although binary complexes with mono- and bifunctional ligands have been studied extensively, a comparable metal–sulfide–thiolate (or related halide) chemistry has (except for the iron–sulfur species)[4–10] not yet been developed. The synthesis and structural determinations of clusters such as $[Co_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$,[5b,11] $[Co_6S_8(PEt_3)_6]^{+1,0}$,[12] and $[Co_8S_6(SPh)_8]^{4-,5-}$[13] or $[Ni_3S(S_2\text{-}o\text{-xyl})_3]^{2-}$,[14] $[Ni_3S(SMe)_6]^{2-}$,[15] and $[Ni_9S_9(PEt_3)_6]^+$[16] present some indication of a growing chemistry based on polyhedral metal–sulfide cores.

Table I. Details of Data Collection and Structure Refinement for $[Ph_4P]_2[Ni_2(S_2)(edt)_4]\cdot MeOH$

formula	$C_{57}H_{60}Ni_4P_2OS_{10}$
mol wt	1373.59
a, Å	11.506 (6)
b, Å	11.902 (6)
c, Å	23.132 (13)
α, deg	104.10 (4)
β, deg	97.23 (4)
γ, deg	105.73 (4)
V, Å^3	2896.6
cryst syst	triclinic
Z	2
d_{calc}, g cm^{-3}	1.58
space group	$P\bar{1}$
cryst dimens	0.2 × 0.15 × 0.1
μ, cm^{-1} (Mo Kα)	17.3
temp, K	150
scan speed, deg/min	4–29
bkgd/scan ratio	0.5
scan mode	$\theta/2\theta$ scan
scan range, deg	$2(\Delta\theta)$ + Kα splitting
$2\theta_{max}$, deg	44
no. of unique data collcd	7161 ($+h,\pm k,\pm l$)
no. of obs data ($I \geq 1.96\sigma(I)$)	5715
no. of variables	699
R/R_w	0.057/0.057

In the course of a systematic investigation of the reaction system Ni(II)/edt^{2-}[3b] in the presence of sulfido or polysulfide species such as S^{2-}, S_2^{2-}, and S_x^{2-}, we have synthesized the novel nickel–disulfide–thiolate cluster $[Ni_4(S_2)(edt)_4]^{2-}$ (**1**), which contains a η^2-S_2 group and thiolate ligands simultaneously. Compounds of this type are most uncommon, the only structurally characterized example besides **1** being $[Mo_3S(S_2)_3(edt)_3]^{2-}$[17] and $[V(S_2)S_2SPh]^{2-}$.[18] We report here the synthetic access to this cluster species by means of a self-assembly reaction from simple reactants

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as well as its crystal structure and its properties in solution. A brief account of our initial results had been presented elsewhere.[19]

Experimental Section

Synthesis. All preparations were carried out under an atmosphere of pure dinitrogen in gloveboxes and Schlenk-type glassware. H_2edt was procured from Jansen Chimica; $NiCl_2$ was purchased from Merck-Schuchardt. Solvents were degassed prior to use. Chemical analyses were performed by the microanalytical laboratories of Beller, Göttingen, FRG, and in the Institute of Organic Chemistry at the University of Münster.

Experimental details concerning the UV/vis spectra, magnetic measurements, and ^1H NMR spectra are given elsewhere.[3b]

$[Ph_4P]_2[Ni_4(S_2)(edt)_4]\cdot MeOH$ (2). A solution of sodium (1.84 g, 80 mmol) and H_2edt (3.34 mL, 40 mmol) in 50 mL of methanol was added to a suspension of $NiCl_2$ (5.18 g, 40 mmol) in 60 mL of methanol. The resulting brown slurry was stirred for 30 min, and solid Na_2S_2 (1.10 g, 10 mmol) was introduced. The brown precipitate dissolved immediately, and a dark brown solution was separated by filtration from a slight quantity of brown amorphous solid. The filtrate was added to solid Ph_4PBr (8.39 g, 20 mmol), and the solution was stored at −30 °C for 3 days. During that time a brown microcrystalline product separated. It was collected by filtration and recrystallized from DMF/MeOH (1:1) to yield 6.5 g (47 %) of dark brown crystals of **2**. UV/vis (DMF): λ_{max} 453 nm (ϵ_M 9000), 354 nm (sh).

Anal. Calcd for $C_{57}H_{60}Ni_4P_2OS_{10}$: C, 49.67; H, 4.39; Ni, 17.03; P, 4.49; S, 23.26. Found: C, 49.93; H, 4.43; Ni, 16.66; P, 3.62; S, 22.72.

X-ray Structure Determination. A single crystal of **2** suitable for X-ray diffraction was isolated from the reaction mixture, fixed with a trace of silicone grease at the top of a glass capillary, and cooled to approximately 150 K under a stream of cold nitrogen gas with a modified Syntex LT-1 low-temperature device. X-ray diffraction data were collected on an automatted Syntex $P2_1$ four-circle diffractometer equipped with a Mo $K\alpha$ source, a graphite monochromator, and a scintillation counter. The unit cell dimensions and their standard deviations were obtained by a least-squares fit of the setting angles of 15 centered reflections in the range $25° < 2\theta < 30°$. Data were collected in the $\theta/2\theta$ scan mode. The intensity of a standard reflection measured every 99 scans did not show any significant changes during the data collection. The intensity profiles of all reflections indicated stable crystal settings during the measurements. Data reduction was done by applying Lorentz and polarization corrections; empirical absorption corrections (ψ scan) were applied. The procedures for data collection and reduction have been described.[3b,7f]

All calculations were done by using the programs of the EXTL and SHELXTL program packages (see ref 3b). Numerical details of the crystal structure analysis, including the final least-squares refinement, are provided in Table I.

Solution and Refinement of the Structure. The calculations were performed on a Data General ECLIPSE S/200 minicomputer. The positions of the nickel and sulfur atoms in the unit cell could be derived from direct methods procedures. The remaining non-hydrogen atom positions were located from difference Fourier maps computed after least-squares refinement cycles. Atomic scattering factors for spherical neutral free atoms (bonded for hydrogen) were taken from standard sources,[20] and anomalous dispersion was taken into account for the non-hydrogen atoms.

Under the given Laue symmetry ($\bar{1}$) the distribution of normalized structure factors indicated the triclinic space group $P\bar{1}$, which was confirmed by the structure solution and successful refinement. The asymmetric unit contains one anion, two cations, and one discrete methanol molecule. Isotropic refinement of all non-hydrogen atoms converged to $R = 0.173$. At this point a positional disorder of the anion became apparent. The anion exists in the crystal lattice in two alternative orientations. Approximately 15% (the minority position set) of the anions are rotated with respect to the majority set of atoms (85%) in such a way that the positions of two nickel atoms and all terminal sulfur atoms coincide in both orientations; e.g., the two alternatively orientated Ni_4S_{10} moieties share a common diagonal. The coinciding positions are occupied by the atoms Ni(1), Ni(3), S(7), S(8), S(9), and S(10). The majority and minority positions for the Ni_4S_{10} frame could be resolved. Their occupancies were refined such that the sum of each corresponding pair was unity, the individual occupancies being 0.15 and 0.85. The positions of the carbon atoms associated with the minority set could not be resolved due to the low scattering power of carbon. The best model included the predominantly occupied atom set as well as the Ni–S frame of the minority set. The final refinement cycles were carried out with anisotropic temperature factors for all non-hydrogen atoms (minority set atoms isotropic). Hydrogen atoms were added as fixed contributions at 0.96 Å from C and with thermal parameters 1.2 times that of the bonded carbon atoms. Positional parameters of the anion are given in Table II, and distances and angles within the Ni–S framework are provided in Table III organized according to the C_{2v} symmetry of the anion. Thermal parameters of the anion, atomic parameters, and complete distances and angles of the anions, cations, and solvate molecules as well as structure factor tables are given in Tables S-I–S-IV (supplementary material).

Table II. $[Ph_4P]_2[Ni_4(S_2)(edt)_4]\cdot MeOH$: Atomic Coordinates of the $[Ni_4(S_2)(edt)_4]^{2-}$ Anion without H Atoms[a]

atom	*x*	*y*	*z*
Ni(1)	0.11265 (9)	0.06599 (8)	0.19316 (4)
Ni(2)	−0.17275 (12)	0.03224 (12)	0.21671 (6)
Ni(2a)	−0.1454 (8)	0.0014 (8)	0.2024 (4)
Ni(3)	−0.07909 (9)	0.18878 (9)	0.33910 (4)
Ni(4)	0.20524 (9)	0.23154 (9)	0.31091 (5)
Ni(4a)	0.1836 (6)	0.2601 (6)	0.3299 (3)
S(1)	0.1130 (2)	0.0318 (2)	0.2831 (1)
S(1a)	0.0058 (11)	−0.0393 (11)	0.2536 (5)
S(2)	−0.0677 (2)	0.0046 (2)	0.2957 (1)
S(2a)	0.0654 (11)	0.0901 (11)	0.3379 (6)
S(3)	−0.0708 (2)	−0.0549 (2)	0.1568 (1)
S(3a)	−0.0772 (13)	−0.0839 (13)	0.1313 (7)
S(4)	−0.2711 (2)	0.0965 (2)	0.2852 (1)
S(4a)	−0.2164 (14)	0.0579 (13)	0.2851 (7)
S(5)	0.1078 (2)	0.2526 (3)	0.3858 (1)
S(5a)	0.1133 (13)	0.3250 (13)	0.4012 (7)
S(6)	0.3054 (2)	0.1750 (2)	0.2411 (1)
S(6a)	0.2496 (16)	0.1567 (14)	0.2561 (7)
S(7)	0.1275 (2)	0.1208 (2)	0.1111 (1)
S(8)	−0.2762 (2)	0.0848 (2)	0.1497 (1)
S(9)	−0.1149 (2)	0.3573 (2)	0.3770 (1)
S(10)	0.2895 (2)	0.4241 (2)	0.3172 (1)
C(1)	−0.1031 (7)	−0.0461 (7)	0.0768 (3)
C(2)	−0.0358 (7)	0.0774 (7)	0.0734 (3)
C(3)	−0.3371 (7)	0.1949 (8)	0.2551 (4)
C(4)	−0.3892 (8)	0.1347 (8)	0.1896 (4)
C(5)	0.1318 (8)	0.4091 (8)	0.4265 (4)
C(6)	0.0569 (11)	0.4676 (8)	0.4058 (6)
C(7)	0.3709 (7)	0.3071 (7)	0.2203 (4)
C(8)	0.3146 (8)	0.4021 (8)	0.2387 (4)

[a] Atoms indicated with an a (i.e. Ni(2a)) belong to the molecular orientation that occurs with 15% probability (see text).

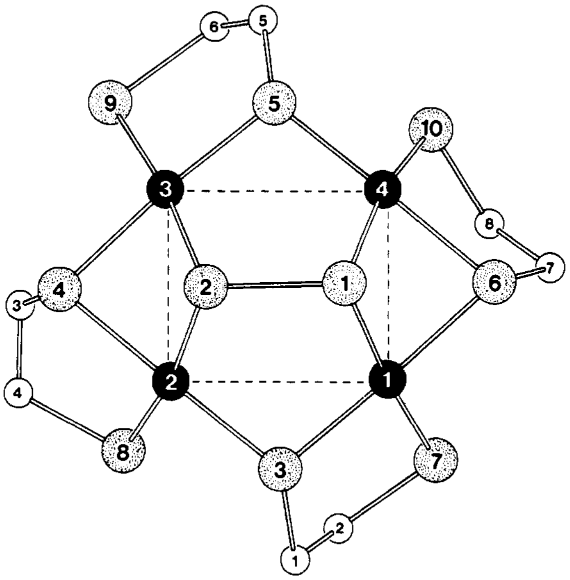

Figure 1. Structure of the $[Ni_4(S_2)(edt)_4]^{2-}$ anion (**1**) with atomic labeling scheme.

Description and Discussion

Crystals of **2** contain isolated anions of **1**, which are separated by Ph_4P^+ cations. The structure of the $[Ni_4(S_2)(edt)_4]^{2-}$ anion (with atomic labeling scheme) is shown in Figure 1.

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Table III. $[Ph_4P]_2[Ni_2(S_2)(edt)_4]\cdot MeOH$: Selected Distances and Angles of the $[Ni_2(S_2)(edt)_4]^{2-}$ Anion

	Distances (Å)		
Ni(1)-Ni(2)	3.329 (2)	Ni(3)–S(2)	2.224 (2)
Ni(1)–Ni(4)	2.822 (1)	Ni(3)–S(4)	2.228 (2)
Ni(2)–Ni(3)	2.869 (1)	Ni(3)–S(5)	2.121 (2)
Ni(3)–Ni(4)	3.344 (2)	Ni(3)–S(9)	2.154 (3)
Ni(1)–S(1)	2.217 (3)	Ni(4)–S(1)	2.215 (2)
Ni(1)–S(3)	2.133 (2)	Ni(4)–S(5)	2.182 (3)
Ni(1)–S(6)	2.225 (2)	Ni(4)–S(6)	2.180 (3)
Ni(1)–S(7)	2.165 (3)	Ni(4)–S(10)	2.194 (2)
Ni(2)–S(2)	2.206 (3)	S(1)–S(2)	2.084 (3)
Ni(2)–S(3)	2.178 (3)		
Ni(2)–S(4)	2.170 (3)		
Ni(2)–S(8)	2.152 (3)		
	Angles (deg)		
Ni(2)–Ni(1)–Ni(4)	89.2 (1)	S(1)–Ni(4)–S(5)	89.8 (1)
Ni(1)–Ni(2)–Ni(3)	91.0 (1)	S(1)–Ni(4)–S(6)	80.4 (1)
Ni(2)–Ni(3)–Ni(4)	88.2 (1)	S(1)–Ni(4)–S(10)	167.6 (1)
Ni(1)–Ni(4)–Ni(3)	91.5 (1)	S(5)–Ni(4)–S(6)	167.5 (1)
S(1)–Ni(1)–S(3)	102.6 (1)	S(5)–Ni(4)–S(10)	99.6 (1)
S(1)–Ni(1)–S(6)	79.4 (1)	S(6)–Ni(4)–S(10)	91.2 (1)
S(1)–Ni(1)–S(7)	173.2 (1)	Ni(1)–S(1)–Ni(4)	79.1 (1)
S(3)–Ni(1)–S(6)	171.1 (1)	Ni(1)–S(1)–S(2)	105.6 (1)
S(3)–Ni(1)–S(7)	93.4 (1)	S(2)–S(1)–Ni(4)	106.9 (1)
S(6)–Ni(1)–S(7)	94.8 (1)	Ni(2)–S(2)–Ni(3)	80.7 (1)
S(2)–Ni(2)–S(3)	90.5 (1)	Ni(2)–S(2)–S(1)	107.1 (1)
S(2)–Ni(2)–S(4)	81.2 (1)	S(1)–S(2)–Ni(3)	105.9 (1)
S(2)–Ni(2)–S(8)	171.0 (1)	Ni(1)–S(3)–Ni(2)	101.1 (1)
S(3)–Ni(2)–S(4)	169.9 (1)	Ni(2)–S(4)–Ni(3)	81.4 (1)
S(3)–Ni(2)–S(8)	97.2 (1)	Ni(3)–S(5)–Ni(4)	102.0 (1)
S(4)–Ni(2)–S(8)	91.7 (1)	Ni(1)–S(6)–Ni(4)	79.7 (1)
S(2)–Ni(3)–S(4)	79.5 (1)		
S(2)–Ni(3)–S(5)	92.4 (1)		
S(2)–Ni(3)–S(9)	172.8 (1)		
S(4)–Ni(3)–S(5)	171.9 (1)		
S(4)–Ni(3)–S(9)	93.4 (1)		
S(5)–Ni(3)–S(9)	94.7 (1)		

Geometrical details are listed in Table II. The metal–sulfide core portion consists of a S_2^{2-} (μ_2-disulfide) group (S–S 2.084 (1) Å) bonded to a rectangular arrangement of nickel atoms in a plane 1.578 Å below it. The metal atoms are bridged by four thiolate sulfur atoms (μ-S, S(3)–S(6)) and terminally coordinated by the atoms S(7)–S(10). Thus, each edt^{2+} ligand furnishes one bridging and one terminal S atom to the M_4S_{10} core portion. The atoms S(3)–S(6) and S(7)–S(10) are situated in two planes (0.171 and 1.675 Å, respectively) below the plane containing the metal atoms, and all three planes are nearly parallel. The anion has an overall C_{2v} symmetry, and its structural features can be described with respect to this symmetry. The average metal–metal distances within the prismane type Ni_4S_2 unit are 2.846 Å (Ni(1)–Ni(4), Ni(2)–Ni(3)) and 3.337 Å (Ni(1)–Ni(2), Ni(3)–Ni(4)), both values being outside the range for direct metal–metal bonding. The metal atoms reside in approximately square-planar sulfur coordination, with the deviation from planarity being 0.001 Å for Ni(1) and Ni(2) and 0.013 and 0.014 Å for Ni(3) and Ni(4), respectively. No other ligand atoms (e.g. from solvate molecules) are within bonding distances to any of the nickel atoms. The mean values of Ni–(S_2) distances (2.216 Å) exceed those of the bridging (2.177 Å) and terminal (2.166 Å) Ni–SR bonds by approximately 0.05 Å. The bridging Ni–SR bonds are decidedly asymmetric, the average values for the individual groups of bonds being 2.150 and 2.203 Å. This graduation suggests a conceptual fragmentation of the $[Ni_4(S_2)(edt)_4]^{2-}$ anion into four Ni(edt) units and one S_2^{2-} group. Moreover, the Ni–(μ-SR) distances can be divided according to the C_{2v} symmetry of the anion. The mean distances within each group are 2.154 Å (S(3)–Ni(1,2), S(5)–Ni(3,4)) and 2.201 Å (S(4)–Ni(2,3), S(6)–Ni(1,4)). The same grouping applies for the corresponding Ni–S_b–Ni angles (80.6 and 101.6°).

From another point of view the Ni_4S_{10} core can be decomposed into alternating Ni_2S_2 and Ni_2S_3 moieties, which are folded along their Ni···Ni diagonals. Each of these units shares two edges with adjacent rings. In addition, the five-membered Ni_2S_3 rings have a common S(1)–S(2) edge.

The Ni_4S_2 core portion of **1** shows a prismane type structure. The structural analogy can be probed by applying electron-counting rules[21] or the isolobal concept.[22] As mentioned above, **1** containing the Ni_4S_2 prismane type unit can conceptually be decomposed into four Ni(edt) fragments and a disulfide group. Since sulfur is isolobal to CH_2, S_2^{2-} is isolobal to $C_2H_4^{2-}$, which can be transformed to $C_2H_2^{4-}$. The Ni(edt) entities can be considered as d^8 ML_2 fragments, which can be substituted by their isolobal CH_2^{2+} or CH^+ equivalents. These fragments are reassembled in order to generate a $C_6H_2^{4-}$ species or the C_6H_6 prismane molecule. Along the same line electron-counting rules that enable predictions to be made concerning the geometries of clusters can be used to confirm these results. These rules tell us that for a trigonal-prismatic cluster of six metal atoms and associated ligands, the appropriate electron count is 90. Replacing two metal atoms by main group elements gives a magic electron count of 90 − (2 × 10) = 70. It can easily be shown that 70 (8 × 4 for Ni^{2+}, 4 × 4 and 4 × 2 for terminal and bridging sulfur atoms, 14 for S_2^{2-}) is the total number of electrons for the Ni_4S_2 core of the $[Ni_4(S_2)(edt)_4]^{2-}$ species. Thus, the Ni_4S_2 framework can be considered a purely inorganic prismane-type analogue.

Compounds simultaneously containing disulfide and thiolate groups coordinated to one metal are most uncommon, the only other structurally characterized examples being $[Mo_3S(S_2)_3(edt)_3]^{2-}$[17] and $[V(S_2)S_2SPh]^{2-}$.[18] In this context it may be worth mentioning that the edt^{2-} group is a common constituent of complexes containing oxidizing ligands (such as S_2^{2-}) as well as of a number of higher oxidation state metal–sulfide–thiolate or metal–thiolate compounds. Examples are $[VS(edt)_2]^{2-}$,[23] $[V_2S_5(edt)]^{3-}$,[18] $[V_2S_4O(edt)]^{3-}$,[18] $[M_2(edt)_4]^{2-}$ (M = Fe, Mn),[24a–d] $[Co(edt)_2]^-$,[24e–g] or $[M_2S_4(edt)_2]^{2-}$ (M = Mo, W),[25] exceptions being $[VS(SPh)_4]^{2-}$[18] and $[V(S_2)S_2SPh]^{2-}$.[18] This concept has been successfully used in our group to generate higher oxidation state main-group complexes such as $[Sn_3S_4(edt)_3]^{2-}$,[26] a main group analogue of $[Mo_3S_4(edt)_3]^{2-}$,[17] whose corresponding monothiolate species are difficult to obtain.

A Ni_4S_{10} structural fragment has not been found previously in any discrete cluster, nor, according to our knowledge, is it in its entirety a portion of the structure of any sulfide mineral. The rectangular arrangement of nickel atoms in the Ni_4S_{10} core bears remote resemblance to the (100) surface of metallic nickel. Electronegative impurities such as chalcogens and halogens are

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known to hinder the chemisorption of small molecules on metal surfaces and to dramatically decrease the rate of catalytic reactions.[27] From a number of experiments the preference for atomic adsorption at the highest coordination site on clean transition-metal surfaces has been established,[28] and specifically, chalcogen adsorption at the nickel (100) 4-fold hollow is well documented.[29] Such 4-fold bridging modes of sulfur (or selenium) are encountered in some molecular compounds, e.g. $[Ni_9S_9(PEt_3)_6]^{2+}$,[16] $[Ni_8Cl_2S_6(PPh_3)_6]$,[29] $[Ni_8S_6(PPh_3)_6]$,[30] $[Ni_8S_5(PPh_3)_7]$,[30] $[Ni_{12}Se_{11}(PPh_3)_8Cl]^{2+}$,[31] and $[Ni_{34}Se_{22}(PPh_3)_{10}]$.[32] A 4-fold coordination of a disulfide group as in $[Ni_4(S_2)(edt)_4]^{2-}$ has not been detected on metal surfaces yet. One might speculate an S_2 group to be existent in the initial reaction steps on sulfided metal surfaces.

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Supplementary Material Available: Thermal parameters of the anion (Table S-I), positional and thermal parameters of the cations and solvate molecules (Table S-II), distances and angles within the cations and solvate molecules (Table S-III), and a stereoscopic view of the $[Ni_4(S_2)(edt)_4]^{2-}$ anion with thermal ellipsoids (Figure S-1) (8 pages); observed and calculated structure factors (Table S-IV) (32 pages). Ordering information is given on any current masthead page.

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Metal–Oxygen Multiple Bond Lengths: A Statistical Study

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The factors that influence metal–oxygen multiple-bond distances have been explored by examining the structures of more than 600 complexes. Mean M–O distances for monooxo compounds have been determined for 11 different metals from titanium to osmium. These mean values decrease on moving from left to right across the periodic table, with the exception of unusually long bonds observed for d^4 octahedral complexes of iron and ruthenium. The bond lengths in di- and trioxo species are on average longer than those in monooxo species, with the general order monooxo < d^0 *cis*-dioxo < *fac*-trioxo < d^2 *trans*-dioxo. For a particular metal, the M–O bond lengths in monooxo compounds fall in a narrow range and describe a fairly smooth and regular distribution. The M–O distance is in general not a sensitive function of the coordination number or the oxidation state of the metal. These observations are discussed with use of simple ligand field descriptions of the metal–oxygen multiple bonds.

The study of compounds with metal–ligand multiple bonds—metal-oxo, -sulfido, -nitrido, -imido, -alkylidyne, -alkylidene, and related complexes—has become one of the fastest growing areas of inorganic chemistry.[1] There is increasing interest in these compounds as reagents or catalysts for organic reactions and as models for the active sites in heterogeneous processes. Oxo, imido, sulfido, and related ligands also appear to be involved in the catalytic cycles of a variety of metalloenzymes, for instance those of cytochrome P-450,[2] nitrogenase,[3] and xanthine oxidase.[4]

Structural studies, in particular single-crystal X-ray diffraction, have played a major role in the development of this area. In most cases a structural study is the primary evidence for a metal–ligand multiple bond, and the bond length is the starting point for a discussion of the nature of the multiple bond. In the course of preparation of a monograph on this topic,[1] a large table has been compiled listing structural data for complexes with metal–oxygen, metal–nitrogen, and metal–carbon multiple bonds; the metal–oxo portion alone contains over 600 structures. The metal–oxo table and accompanying references are available as supplementary material, and the whole table appears in the monograph.

In this report, the wealth of data in the table is used to explore some of the factors that influence metal–oxygen multiple-bond distances. The importance of the nature of the metal, its oxidation state and coordination number, and the formal M–O bond order have been examined. Because of the large number of structures (290 for molybdenum alone!), the data have been analyzed with use of simple statistical procedures.

Results and Discussion

Methodology. The structural data used in this study derive primarily from X-ray crystallography, with a few structures determined by electron diffraction or microwave spectroscopy. Only terminal oxo complexes are considered; bridged species, heteropolyanions, and nonmolecular structures (e.g. MoO_3) have in general not been included. For each complex the data tabulated include the metal–oxygen multiple-bond length and its estimated standard deviation (σ)[5] and the coordination number[6] and oxidation state of the metal center.[7]

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(6) The coordination number is defined in the usual fashion, with the following special cases: cyclopentadienyl groups are counted as tridentate ligands, peroxide (O_2^{2-}) and related species as bidentate ligands, and olefin and acetylene as monodentate ligands.

(7) The table also includes information about the angle(s) cis to the multiply bonded ligand and references.