as defined by the metal and oxygen atom positions is expected to be well established.

Acknowledgment. This research has been supported financially by the Swedish Natural Science Research Council.

Registry No. $Ni_5Sb_3O_2(OEt)_{15}(HOEt)_4$, 140872-93-1.

Supplementary Material Available: A table of crystallographic data, listings of anisotropic thermal parameters for the non-hydrogen atoms, positional and isotropic thermal parameters for the hydrogen atoms, calculated bond distances, angles, and planes, and figures showing the molecular packing in the crystal structure (8 pages); a table of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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Studies on the Reactivity of S,N-Derivatives of Nickel with N-Donor Bases. Crystal Structure and Magnetic Properties of the Cubane Cluster Tetrakis(μ-hydroxo)tetrakis(μ-1,3-thiazolidine-2-thionato)tetrakis(pyridine)-tetranickel(II)–Dipyridine

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Received June 5, 1991

The reaction of polymeric $[Ni(tzdt)_2]$ (tzdt = 1,3-thiazolidine-2-thionate) with pyridine affords two different compounds depending on the conditions employed: $[Ni(tzdt)_2(py)_2]$ in dry pyridine and $[Ni_4(OH)_4(tzdt)_4(py)_4]\cdot 2py$ with an excess of water. The former, mononuclear and paramagnetic, shows the nickel atom in an octahedral environment, while the latter has a cubanelike structure crystallizing in the tetragonal system: space group $P\bar{4}2_1c$, $Z = 8$, $a = 11.969$ (5) Å, $c = 18.357$ (9) Å, and $V = 2629$ (2) Å^3. The magnetic susceptibility of this cubane has been measured in the range 295–4 K showing that the compound has a diamagnetic ground state. The magnetic exchange among the four nickel atoms has been modeled with the use of three parameters, four ferromagnetic interactions ($J_1 = 17.5$ cm^{-1}) and two antiferromagnetic ($J_2 = J_3 = -22$ cm^{-1}). These interactions are propagated by the hydroxo bridges and are dependent on the Ni–O–Ni angles. The antiferromagnetic behavior is explained in terms of the distortions induced in the cubane core by the tzdt bridging ligands leading to two different types of Ni–O–Ni, those of ca. 95–96° and those of 103°. It is proposed that the latter are associated with the antiferromagnetic couplings.

Introduction

In previous papers we have described the coordinative ability of anionic sulfur-donor ligands in nickel(II) complexes and their reactivity toward N- and P-donor bases,[1] the nature of the obtained species being dependent on the sulfur ligand and the Lewis base.

1,3-Thiazolidine-2-thione (tzdtH), that exists mainly in the thione form in neutral solutions, is also of interest because of the possibility of coordination as a unidentate, bidentate, or bridging ligand.[2] The bridge form has been found in diamagnetic $[Ni(tzdt)_2]$ with a polymeric square-planar structure.[3] This ability can be used to obtain polynuclear nickel(II) complexes, with magnetic exchange interactions, in particular nickel(II) tetramers with cubanelike $[Ni_4O_4]$ cores.[4–6]

In our studies on the reactivity of $[Ni(tzdt)_2]$ toward N-donors we have obtained a mononuclear $[Ni(tzdt)_2(py)_2]$ compound and a tetrameric hydroxo complex $[Ni_4(OH)_4(tzdt)_4(py)_4]\cdot 2py$. To our knowledge this is the first tetranuclear hydroxo–nickel complex. The other tetranuclear complexes of nickel consist of a $[Ni_4(OCH_3)_4]^{4+}$ cubane framework. Most of these exhibit ferromagnetic intracluster exchange interactions, a result that has been attributed to the fact that the bridge angles Ni–O–Ni are close to 90° (in the range 93–99°).[4,5] The only exception to this behavior has been found in the complex $[Ni_4(OMe)_4(O_2CMe)_2(tmb)_4]^{2+}$,[6] (tmb = 2,5-dimethyl-2,5-diisocyanohexane) which exhibits an overall antiferromagnetic behavior that has been attributed to the presence of bridge angles of ca. 101°. We present here the crystal structure and magnetic properties of $[Ni_4(OH)_4(tzdt)_4(py)_4]\cdot 2py$. The magnetic properties of this compound are also dominated by an antiferromagnetic exchange interaction as a consequence of the presence of unusual bridge angles of ca. 103° in the cubane cluster.

Experimental Section

Materials and Methods. 1,3-Thiazolidine-2-thione was purchased from Ega Chemie and recrystallized from hot water before use. Pyridine was supplied by Merck and distilled over sodium. $[Ni(tzdt)_2]$ was prepared according to a previously reported procedure.[3]

Elemental analyses were carried out by the Servicio de Microanálisis of the Universidad Complutense de Madrid. IR spectra were taken in KBr disks using a Perkin-Elmer 1300 or a Philips PU9712 spectrophotometer. Electronic spectra were recorded in solids using a Uvikon 620 spectrophotometer equipped with diffuse reflectance accessories. Magnetic measurements were carried out with a Faraday-type susceptometer equipped with a helium continuous-flow cryostat.

Preparation of Compounds. Bis(1,3-thiazolidine-2-thionato)bis(pyridine)nickel(II), $[Ni(tzdt)_2(py)_2]$. $[Ni(tzdt)_2]$ (0.5 mmol) was dissolved in 5 mL of pyridine and the solution was stirred for 1 h, forming the adduct as a green microcrystalline solid that precipitated completely by addition of diethyl ether to the pyridine solution. The solid was collected, washed with a pyridine/diethyl ether mixture, and dried in vacuo. A quantitative yield was obtained.

Anal. Calc for $C_{16}H_{18}N_4NiS_4$: C, 42.4; H, 3.9; N, 12.4. Found: C, 42.4; H, 3.9; N, 12.0. IR (cm^{-1}): 3040 (w), 2920 (w), 2850 (m), 1600 (s), 1506 (s), 1480 (m), 1440 (s), 1295 (s), 1215 (s), 1070 (s), 1024 (s), 978 (s), 930 (m), 755 (s), 690 (s), 660 (m), 625 (m), 435 (m). UV–vis (nm): 760, 610, 360, 300, 212.

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Table I. Crystal and Refinement Data for $[Ni(OH)(tzdt)(py)]_4 \cdot 2py$

formula in asymmetric unit	$NiS_2ON_2C_8H_{10} \cdot {}^1/_2C_5H_5N$
fw	312.43
cryst syst	tetragonal
space group	$P\bar{4}2_1c$
a, Å	11.969 (5)
c, Å	18.357 (9)
V, Å^3	2629 (2)
Z	8
ρ(calcd), g cm^{-3}	1.57
temp, °C	21
μ, cm^{-1}	17.71
λ(graphite-monochromated Mo Kα radiation), Å	0.710 69
R(int), %	1.8
R_F,[a] %	4.8
R_{wF},[a] %	4.9

[a] $R_F = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_{wF} = [\sum(|F_o| - |F_c|)^2]^{1/2}$.

Table II. Atomic Parameters for $[Ni(OH)(tzdt)(py)]_4 \cdot 2py$ and Thermal Parameters as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i \cdot \mathbf{a}_j$

atom	x/a	y/b	z/c	U_{eq}
Ni	0.6338 (2)	0.4921 (2)	0.5560 (1)	381 (7)
S1	0.6357 (5)	0.2225 (4)	0.4543 (4)	562 (19)
S2	0.8577 (5)	0.1785 (5)	0.5165 (3)	634 (21)
N1	0.7495 (13)	0.3606 (14)	0.5449 (11)	463 (56)
N2	0.6484 (14)	0.4837 (18)	0.6716 (7)	501 (59)
O1	0.5054 (12)	0.6060 (8)	0.5557 (5)	382 (32)
C1	0.7425 (16)	0.2704 (16)	0.5102 (11)	416 (64)
C2	0.8549 (19)	0.3685 (21)	0.5843 (11)	687 (83)
C3	0.9308 (18)	0.2771 (23)	0.5735 (18)	901 (119)
C4	0.6677 (28)	0.5771 (24)	0.7108 (13)	783 (111)
C5	0.6815 (35)	0.5695 (37)	0.7856 (16)	1139 (170)
C6	0.6679 (42)	0.4652 (41)	0.8197 (12)	1369 (202)
C7	0.6465 (27)	0.3778 (30)	0.7806 (15)	941 (132)
C8	0.6371 (23)	0.3886 (22)	0.7047 (12)	679 (94)
N3	0.0000 (0)	0.5000 (0)	0.2564 (0)	1265 (59)
C9	0.0957 (0)	0.5162 (0)	0.2864 (0)	1277 (55)
C10	0.1007 (0)	0.5136 (0)	0.3535 (0)	1404 (54)
C11	0.0000 (0)	0.5000 (0)	0.3854 (0)	1256 (73)

Tetrakis(μ-hydroxo)tetrakis(μ-1,3-thiazolidine-2-thionato)tetrakis(pyridine)tetranickel(II)–Dipyridine, $[Ni_4(OH)_4(tzdt)_4(py)_4] \cdot 2py$. A suspension of $[Ni(tzdt)_2]$ (0.5 mmol) in a mixture of pyridine (8 mL)/water (4 mL) was stirred for 20 h. The blue-green solid formed was filtered off, washed with water, and dried in vacuo. The yield was quantitative.

Anal. Calc for $C_{42}H_{50}N_{10}Ni_4O_4S_8$: C, 40.3; H, 4.0; N, 11.2. Found: C, 40.7; H, 3.9; N, 11.1. IR (cm^{-1}): 3640 (m), 3030 (w), 2920 (w), 2830 (m), 1585 (s), 1565 (m), 1489 (s), 1470 (m), 1430 (s), 1290 (s), 1200 (s), 1135 (m), 1055 (m), 1015 (s), 962 (s), 929 (s), 740 (m), 680 (s), 645 (s), 420 (m), 365 (m). UV–vis (nm): 785, 610, 520, 370, 300, 212.

Crystal Data for $[Ni_4(OH)_4(tzdt)_4(py)_4] \cdot 2py$. Well-formed green crystals were obtained by slow evaporation of a pyridine/water (2:1) solution at room temperature. A summary of the fundamental crystal data is given in Table I. A green crystal of prismatic shape was resin epoxy coated and mounted in a κ diffractometer. The cell dimensions were refined by least-squares fitting the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ni and S were taken from ref 7. The structure was solved by Patterson and Fourier methods. An empirical absorption correction[8] was applied at the end of the isotropic refinement.

The atoms of the crystallization pyridine ring were located in a difference synthesis. Because of some nonresolvable disorder of this group, the refinement was carried out with fixed coordinates and isotropic thermal parameters for N3, C9, C10, and C11.

After several cycles of mixed refinement, the H1 atom was located in a difference synthesis as the highest peak of the map. No trend in F vs F_o or $(\sin \theta)/\lambda$ was observed. Final refinement with fixed isotropic factors and coordinates for H atoms led to $R = 4.8$ and $R_w = 4.9$.

Refined atomic coordinates are given in Table II. Structure factor amplitudes are supplied as supplementary material. Most of the calculations were carried out with the X-ray 80 system.[9]

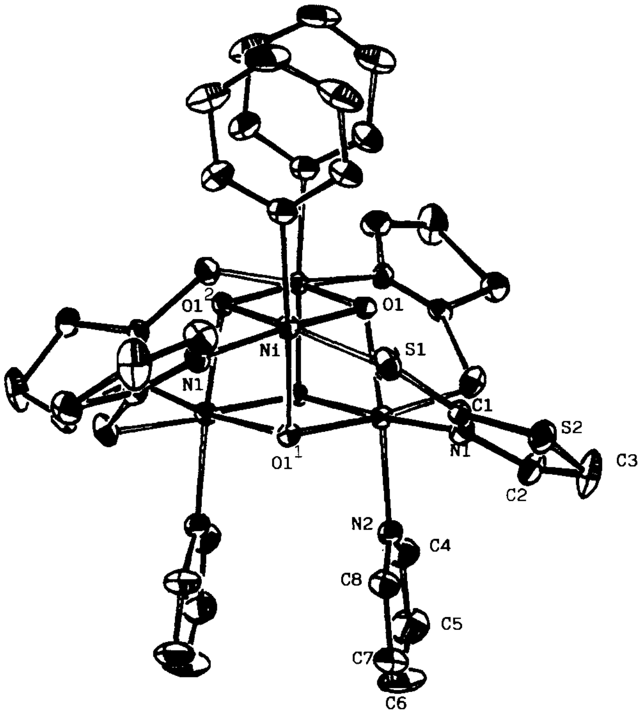

Figure 1. Perspective ORTEP view of the tetrameric unit with atomic numbering scheme. H atoms are omitted, and thermal ellipsoids are at 50% probability level.

Results and Discussion

In the reaction of $[Ni(tzdt)_2]$ with pyridine two different compounds are obtained, depending on the reaction conditions. When dry pyridine is used, a green powder that analyzes for $[Ni(tzdt)_2(py)_2]$ is obtained, whereas in pyridine/water the product is blue-green $[Ni_4(OH)_4(tzdt)_4(py)_4] \cdot 2py$.

The formation of the monomeric adduct implies the change in the tzdt coordination from bridging to bidentate, although the similarities of the IR spectrum with that of the starting complex suggests the coordination via nitrogen and exo sulfur to the metal. This coordination gives an additional strain to the four-membered chelate ring that explains its instability and easy decomposition to the starting $[Ni(tzdt)_2]$ in absence of pyridine.

Spectroscopic Properties. The UV–vis spectra of both the monomeric and tetrameric complexes are consistent with a distorted-octahedral environment of a hexacoordinated nickel(II). For monomeric $[Ni(tzdt)_2(py)_2]$ the frequency and intensity of the observed bands are consistent with a tetragonal distortion in the octahedral complex similar to that proposed for $[Ni(MBT)_2L_2]$, where MBT = 2-mercaptobenzothiazolate.[10]

The IR spectra of both complexes show the characteristic thioamide bands at ca. 1500 (thioamide I), 1250 (thioamide II), and 980 cm^{-1} (thioamide III). The shifts of these bands relative to the free neutral ligand clearly indicate the coordination of the nitrogen and the exocyclic sulfur to the metal.[3] In addition, the IR spectrum of the cubane shows a sharp absorption at 3640 cm^{-1} that can be assigned to the bridging OH group.

Crystal Structure of $[Ni_4(OH)_4(tzdt)_4(py)_4] \cdot 2py$. The structure of $[Ni_4(OH)_4(tzdt)_4(py)_4] \cdot 2py$ shows the formation of tetrameric μ-hydroxo units (Figure 1).[11] Each nickel is in a distorted-octahedral environment that includes three hydroxide oxygen atoms, one pyridine nitrogen, and one nitrogen and one sulfur atom belonging to different tzdt groups. These tzdt groups bridge two metal atoms via nitrogen and exo sulfur (S1).

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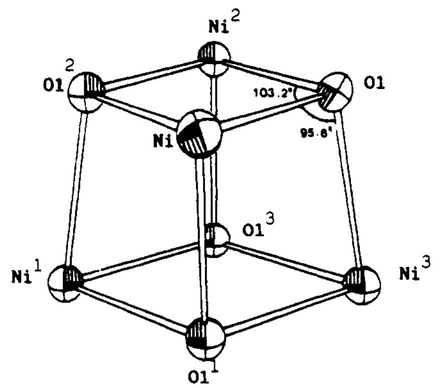


Figure 2. ORTEP view and atom-labeling of the $[Ni_4O_4]$ core of $[Ni_4(OH)_4(tzdt)_4(py)_4]\cdot 2py$.

Table III. Selected Interatomic Distances (Å) and Angles (deg) for $[Ni(OH)(tzdt)(py)]_4\cdot 2py$ with Esd's in Parentheses[a]

Ni-N1	2.11 (2)	N1-C2	1.46 (3)
Ni-N2	2.13 (1)	N2-C4	1.35 (3)
Ni-O1	2.05 (1)	N2-C8	1.30 (3)
Ni-O1(1)	2.08 (1)	C2-C3	1.44 (3)
Ni-O1(2)	2.04 (1)	C4-C5	1.39 (4)
Ni-S1	2.44 (1)	C5-C6	1.41 (6)
S1-C1	1.74 (2)	C6-C7	1.29 (5)
S2-C1	1.77 (2)	C7-C8	1.40 (4)
S2-C3	1.80 (3)	Ni-Ni(1)	3.06 (4)
N1-C1	1.26 (3)	Ni-Ni(2)	3.20 (3)
N1-Ni-O1	170.9 (6)	C1-S2-C3	91 (1)
N1-Ni-O1(1)	91.2 (6)	Ni-N1-C2	118 (1)
N1-Ni-O1(2)	96.1 (6)	Ni-N1-C1	130 (1)
N1-Ni-N2	90.4 (7)	C1-N1-C2	111 (2)
N1-Ni-S1	93.2 (5)	Ni-N2-C8	120 (1)
N2-Ni-O1	95.5 (6)	Ni-N2-C4	120 (1)
N2-Ni-O1(1)	175.1 (6)	C4-N2-C8	120 (2)
N2-Ni-O1(2)	92.4 (6)	S2-C1-N1	117 (1)
N2-Ni-S1	93.0 (6)	S1-C1-N1	129 (1)
O1-Ni-O1(1)	82.4 (5)	S1-C1-S2	114 (1)
O1-Ni-O1(2)	76.8 (4)	N1-C2-C3	115 (2)
O1-Ni-S1	93.4 (4)	S2-C3-C2	106 (2)
O1(1)-Ni-O1(2)	82.8 (4)	N2-C4-C5	120 (3)
O1(1)-Ni-S1	91.5 (4)	C4-C5-C6	119 (3)
O1(2)-Ni-S1	169.2 (4)	C5-C6-C7	120 (3)
Ni-O1-Ni(2)	103.2 (4)	C6-C7-C8	119 (3)
Ni-O1-Ni(3)	95.6 (4)		
Ni(2)-O1-Ni(3)	96.1 (5)		

[a] Symmetry transformations: (1), $(y, 1-x, 1-z)$; (2) $(1-x, 1-y, z)$; (3) $(1-y, x, 1-z)$.

The four nickel and four hydroxo groups are in the alternate corners of a distorted cube (Figure 2). These tetrameric units are generated by the $\bar{4}$ axis in the *c* direction passing through the center of the cubane unit.

The main interatomic distances and angles are summarized in Table III. All the Ni-O distances are slightly larger than those reported in the few (μ_3-hydroxo)nickel complexes found in the literature,[12] but in the range (2.02-2.12 Å) of the Ni-OMe distances in other cubane clusters.[4,5,13] The nickel-nitrogen and nickel-sulfur distances lie in the normal range for nickel(II) complexes.

The tzdt groups bridge the nickel atoms on the four faces parallel to the *c* axis, with a Ni-Ni distance of 3.06 (4) Å. The remaining Ni-Ni distances are 3.20 (3) Å, giving rise to a distorted Ni_4O_4 (Figure 2). Two types of Ni-O-Ni angles are also observed. In the four faces of the cube containing the tzdt ligands, the angles are ca. 96° whereas in the other two faces these angles are 103.2 (4)°.

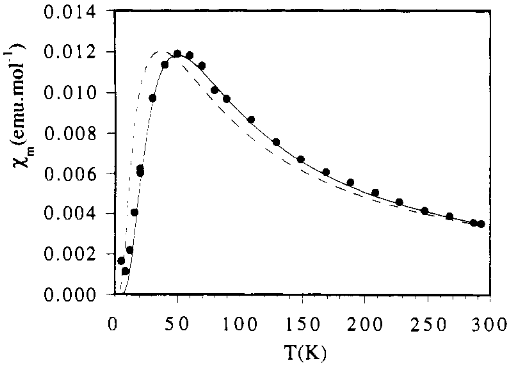
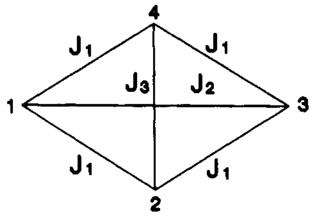


Figure 3. Plot of χ_m vs temperature for $[Ni_4(OH)_4(tzdt)_4(py)_4]\cdot 2py$: experimental values (●); calculated values for the cubane model (—); calculated values for a noninteracting dimer model (---).

Chart I



The Ni-Ni distances mentioned above are in the range expected for nickel atoms bonded by bridging ligands and eliminate the possibility of direct metal-metal interaction since these are considerably longer than the interatomic distances in nickel metal (2.44 Å).

The main feature in the tzdt ligands is the short C-N distance, 1.26 (2) Å, indicating a localization of the double bond between these atoms and the single character of the C-S bond, 1.74 (2) Å due to coordination. Similar values were found in other metal-tzdt complexes,[14] while values for intermediate bond orders are reported for the analogous free ligand benzo-1,3-thiazolidine-2-thione.[15]

Magnetic Properties. The compound $[Ni(tzdt)_2(py)_2]$ is paramagnetic and shows an effective magnetic moment of 3.53-3.40 μ_B in the range 279-68 K, consistent with a mononuclear hexacoordinate nickel(II) complex.

In the tetrameric compound the magnetic susceptibility per nickel(II) ion vs temperature is illustrated in Figure 3. An antiferromagnetic behavior with a maximum in χ_m about 60 K and a sharp decrease at lower temperatures is observed, indicating that the compound has a diamagnetic ground state. This is in contrast to the usual ferromagnetic spin coupling reported in most of the other nickel tetramers.[4,5] In view of the good magnetic isolation of the cubane cluster provided by both tzdt and pyridine ligands, this behavior arises from the intracluster Ni-Ni-exchange interactions.

In general, the spin Hamiltonian appropriate for the exchange interaction of a four-spin $S = 1$ cubane cluster can be written as

$$\mathcal{H} = -2J_1(S_1S_2 + S_2S_3 + S_3S_4 + S_1S_4) - 2J_2S_1S_3 - 2J_3S_2S_4$$

where J_1, J_2, and J_3 correspond to the three types of exchange interactions as a consequence of the distortions of the cluster and S_1, S_2, S_3, and S_4 are the spin operators associated with the nickel(II) ions according to the numbering scheme shown in Chart I.

This Hamiltonian can be solved exactly using the vector coupling methods of Kambe to obtain the energies of the different spin states and, subsequently, a close expression of the magnetic susceptibility.[6] The magnetic susceptibility data for $[Ni_4(OH)_4(tzdt)_4(py)_4]$ were analyzed in terms of this cubane model.

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An excellent fit was obtained from the following set of parameters: $J_1 = 17.5$ cm^{-1}, $J_2 = J_3 = -22$ cm^{-1}, $g = 2.0$ (solid line of Figure 3). The fitted g value seems too low, but in other similar nickel clusters a value of 2.00 has also been found.[6] To confirm the validity of this fit, in particular the presence of ferromagnetic exchange interactions, the data were fit to a noninteracting dimer model (i.e. J_1 was set to be 0) giving $J = -12.5$ cm^{-1} and $g = 2.05$. As can be seen in Figure 3 (dashed line) this model is completely unable to reproduce the position of the maximum in χ_m. Therefore, the exchange network of this cluster is formed by four ferromagnetic exchange interactions (J_1) and two antiferromagnetic ones (J_2 and J_3).

The different sign of these interactions can be attributed to the presence of two types of Ni–O–Ni angles as a consequence of the distortions within the [Ni_4O_4] unit produced by the bridging tzdt molecules. Thus, in the four faces of the cube containing tzdt ligands the Ni–O–Ni angles (95–96°) are in the range in which the Ni–Ni-exchange interactions are ferromagnetic.[4] In the other two faces the Ni–O–Ni angles are 103°. These angles are unusually large for a cubane framework, giving rise to a resultant antiferromagnetic exchange interaction. There is only one other example, $[Ni_4(OMe)_4(O_2CMe)_2(tmb)_4]^{2+}$,[6] in which similar distortions in the cubane framework have been found. In this complex, the presence of two bridging acetates leads to two ferromagnetic exchange interactions (=18 cm^{-1}), associated with Ni–O–Ni angles of ca. 93°, and to four antiferromagnetic ones (≈–9 cm^{-1}), associated with angles of ca. 101°. A comparison of the exchange parameters of this compound with those found in $[Ni_4(OH)_4(tzdt)_4(py)_4]$ allow us to notice that while the ferromagnetic exchange interaction is similar in both compounds, the antiferromagnetic one is significantly stronger in the latter (–22 compared to –9 cm^{-1}). This result emphasizes the sensitivity of the antiferromagnetic exchange interactions with respect to the Ni–O–Ni angles.

Acknowledgment. The Comisiôn Interministerial de Investigaciôn is gratefully acknowledged for financial support, Projects PS87-0028, MAT89-177 (E.C.), and MAT88-0250-C02-C01 (A.M.).

Registry No. $[Ni(tzdt)_2]$, 30798-12-0; $[Ni(tzdt)_2(py)_2]$, 140875-45-2; $[Ni_4(OH)_4(tzdt)_4(py)_4]\cdot 2py$, 140875-47-4.

Supplementary Material Available: Tables of complete crystal and refinement data, calculated atomic coordinates and anisotropic thermal parameters, and bond distances and angles (6 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Group VI Metal Carbonyl Tellurides: Structures of $[M_4(CO)_{18}(\mu_3\text{-}Te)_2]^{2-}$ (M = Cr, W), $[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_2)]^{2-}$, and $[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_3)]^{2-}$

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Received August 22, 1991

The reactions of group 6 metal carbonyls with soluble polytellurides, Te_x^{2-} ($x = 1$–4), have been investigated using a 3-fold excess of the metal carbonyls. Several novel products have been isolated and characterized as their PPh_4^+ salts, including $[M_4(CO)_{18}(\mu_3\text{-}Te)_2]^{2-}$, (M = Cr, Mo, W), $[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_2)]^{2-}$, and $[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_3)]^{2-}$. The reaction of Te_2^{2-} with 3 equiv of $M(CO)_6$ generates $[M_4(CO)_{18}(\mu_3\text{-}Te)_2]^{2-}$ in good yield. The molecule contains a four-membered M_2Te_2 ring with a transannular metal–metal bond, which renders the molecules diamagnetic. One remaining lone pair on each of the Te atoms is donated to an out of plane $M(CO)_5$ fragment. The ring metal atoms are formally oxidized to M(I) states. Reaction of Te^{2-} with excess $Cr(CO)_6$ leads to formation of $[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_2)]^{2-}$, which contains four $Cr(CO)_5$ fragments bound to lone pairs on a Te_2^{2-} chains. Reaction of any long chain Te_x^{2-} fragment, where $x \geq 3$, with excess $Cr(CO)_6$ leads to formation of $[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_3)]^{2-}$, containing a Te_3^{2-} chain with two $Cr(CO)_5$ fragments bound to lone pairs on each terminal tellurium. Two polymorphs of this anion have been isolated and characterized. No evidence of similar reactivity could be obtained with $W(CO)_6$ or $Mo(CO)_6$. All compounds have been characterized by IR and ^{125}Te NMR spectroscopy in addition to single-crystal diffraction. Structural data: for $[(C_6H_5)_4P]_2[W_4(CO)_{18}(\mu_3\text{-}Te)_2]$ (I), triclinic, $P\bar{1}$, $a = 10.026$ (4) Å, $b = 12.411$ (4) Å, $c = 14.404$ (5) Å, $\alpha = 81.21$ (3)°, $\beta = 87.45$ (3)°, $\gamma = 69.28$ (3)°, $V = 1657$ (1) Å^3, $Z = 1$, $R(F_o) = 0.0266$; for $[(C_6H_5)_4P]_2[Cr_4(CO)_{18}(\mu_3\text{-}Te)_2]$ (II), triclinic, $P\bar{1}$, 10.039 (3) Å, $b = 12.287$ (4) Å, $c = 14.275$ (5) Å, $\alpha = 81.54$ (3)°, $\beta = 88.00$ (3)°, $\gamma = 70.14$ (3)°, $V = 1637.9$ (9) Å^3, $Z = 1$, $R(F_o) = 0.0382$; for $[(C_6H_5)_4P]_2[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_2)]\cdot CH_2Cl_2$ (III), triclinic, $P\bar{1}$, $a = 11.753$ (6) Å, $b = 12.656$ (7) Å, $c = 26.670$ (15) Å, $\alpha = 76.63$ (4)°, $\beta = 85.30$ (4)°, $\gamma = 70.78$ (4)°, $V = 3644$ (3) Å^3, $Z = 2$, $R(F_o) = 0.0482$; for $[(C_6H_5)_4P]_2[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_3)]$ (IVa), triclinic, $P\bar{1}$, $a = 10.610$ (3) Å, $b = 13.890$ (4) Å, $c = 14.425$ (4) Å, $\alpha = 115.14$ (2)°, $\beta = 91.98$ (2)°, $\gamma = 106.83$ (2)°, $V = 1812$ (1) Å^3, $Z = 1$, $R(F_o) = 0.0395$; for $[(C_6H_5)_4P]_2[Cr_4(CO)_{20}(\eta^2\text{-}\mu_2\text{-}Te_3)]\cdot CH_2Cl_2$ (IVb), orthorhombic, $Pbca$, $a = 14.557$ (3) Å, $b = 29.074$ (8) Å, $c = 35.995$ (8) Å, $V = 15234$ (16) Å^3, $Z = 8$, $R(F_o) = 0.0872$.

Introduction

Historically the chemistry of transition metal complexes containing telluride ligands has been a relatively unexplored area, although recently the chemistry has been expanding very quickly.[1-4] This is due in part to the use of metal telluride clusters as sources of new solid-state materials.[5] In addition, the enormous role of sulfide atoms[6] and other p-block elements[7] in cluster building suggests that the heavy chalcogenides would also be suitable for this purpose.[8] Recent results show that tellurides are quite active in metal cluster building reactions[9] but that they often display chemistry considerably different from that displayed by sulfides due to the large size, increased nucleophilicity, and

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