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Structure of a Lead(II) Salt of Ethane-1,2-dithiol, a Simple Analogue of Therapeutic Chelating Dithiols

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Crystals of lead(II) ethane-1,2-dithiolate, Pb(edt), of a quality suitable for diffraction studies have been prepared from a mixture of Pb^{2+} and an excess of the thiolate anion. The compound crystallizes in the orthorhombic space group *Pbca*, with eight formula units in a unit cell of dimensions $a = 7.458$ (1), $b = 13.785$ (2), and $c = 9.604$ (1) Å. The structure has been refined by full-matrix least-squares techniques on F using 1079 observations with $F_o > 3\sigma(F_o)$ to an agreement factor $R = 0.040$. The crystals are built up from polymeric sheets of Pb atoms, sandwiched between layers of S atoms, with the sheet periphery formed by a hydrocarbon layer. Each Pb atom is coordinated to one edt entity with Pb–S distances of 2.655 (3) and 2.660 (3) Å and interacts with two other S atoms at 3.032 (3) and 3.056 (3) Å and two further S atoms at 3.376 (3) and 3.584 (3) Å. The coordination geometry so formed is that of a distorted octahedron; however, one large S–Pb–S angle of 128.17 (8)° suggests that a lone pair of lead electrons is stereochemically active, in which case the coordination geometry is best described as pentagonal bipyramidal with the lone pair in an equatorial site, the kernel being of VSEPR type AX_6E.

Introduction

Although simple lead(II) thiolates, $Pb(SR)_2$, have been known for many years, there are few structural data available for this class of compounds; most attempts at crystallographic characterization of such thiolates have been frustrated by their very low solubility in noncoordinating solvents, which has been attributed to a polymeric structure.[1] However, in recent years success has been achieved both in reducing the polymerization of the salts by the use of thiols with bulky substituents[2] and in increasing their solubility in semipolar media by substitution of hydrophilic groups in the thiolate ligand.[3]

In work from one of our laboratories[4] it has been shown that many lead thiolates dissolve in methanol in the presence of an excess of the corresponding sodium thiolate. The soluble species are (thiolato)plumbates(II), as shown by our recent structural characterization[5] of $[(C_6H_5)_4As][Pb(SC_6H_5)_3]$ (along with the selenium analogue). More lately we have found that crystals of lead thiolates of a quality suitable for diffraction studies can often be grown from Pb^{2+}–SR^- or $Pb(SR)_2$–SR^- mixtures,[6] and in particular, we have obtained in this manner a crystalline sample of lead(II) ethanedithiolate.

The structure of lead(II) ethane-1,2-dithiolate, Pb(edt) (**1**), is of considerable interest, not only because there is at present no reported structure of a dithiolate of lead(II) but also because ethanedithiol is a simple analogue of both 2,3-dimercapto-1-propanol (also called British antilewisite, BAL) and sodium 2,3-dimercapto-1-propanesulfonate (DMPS), which are used for the treatment of lead intoxication.[7,8] The interaction of these therapeutic agents with lead(II) on a molecular level is not well understood, though there is evidence that the $-OH$ and $-SO_3^-$ groups are not strongly involved in binding to lead.[4] We therefore report herein the results of a single-crystal X-ray analysis of Pb(edt) (**1**), in which a simple chelating dithiol is coordinated to a Pb atom.

Experimental Section

All chemicals were of reagent grade and were used as received. Carbon and hydrogen elemental analyses were performed by Guelph Chemical Laboratories Ltd., and Pb(II) was determined by EDTA titration using xylenol orange indicator.[9]

Table I. Crystal Data and Experimental Conditions

compd	$C_2H_4S_2Pb$
fw	299.372
cryst syst	orthorhombic
space group	*Pbca* (No. 61)
unit cell dimens, Å	$a = 7.458$ (1) $b = 13.785$ (2) $c = 9.604$ (1)
cell vol, Å^3	986.93
temp, °C	23
Z; $F(000)$	8; 1040.0 e
density, g·cm^{-3}: obsd; calcd	4.0 (1); 4.028
cryst dimens, mm	0.13 × 0.13 × 0.11
cryst faces	{111}, {010}
radiation; wavelength, Å	Mo Kα; $\lambda = 0.71073$
abs coeff, cm^{-1}	350.81
Gaussian grid	14 × 8 × 18
transmissn factors: max; min	0.1149; 0.0474
detector aperture, mm: vert; horiz	4.0; 6.0 + 0.35 tan θ
cryst–detector dist, mm	205
takeoff angle, deg	2.5
scan mode	θ–2θ
scan width, deg	0.6 + 0.35 tan θ
data collcd	$1 \le 2\theta \le 70$; $0 \le h \le 12$, $0 \le k \le 22$, $-15 \le l \le 0$

Crystals of **1** were obtained during an attempted synthesis of $(Me_4N)_2[Pb(edt)_2]$, which was carried out under an argon atmosphere in a glovebag with solvents that had been thoroughly deoxygenated with argon.

Sodium ethanedithiolate (Na_2edt) was prepared in situ in 20 mL of methanol from 1.12 g (12 mmol) of $edtH_2$ and 0.55 g (24 mmol) of Na and added with stirring to 1.9 g (6 mmol) of $Pb(NO_3)_2$ in 15 mL of water, giving a light yellow precipitate. After 5 min, a solution containing 1.45 g (13 mmol) of Me_4NCl in 15 mL of MeOH was added, followed by 100 mL of CH_3CN. The mixture was brought to boiling and filtered hot, after which the filtrate was again brought to boiling, allowed to cool to room temperature, sealed, and refrigerated. A mixture of light yellow crystals of Pb(edt) and near-colorless crystals of an as yet unidentified product was formed; the crystalline material was isolated by decantation, washed with water and methanol, and dried in argon. The crystals were separated by handpicking. Anal. Calcd for $C_2H_4S_2Pb$: C, 8.02; H, 1.35; Pb, 69.21. Found: C, 8.42; H, 1.52; Pb, 69.35.

Collection and Reduction of X-ray Data

Well-developed, pale yellow crystals of equant habit were chosen. A preliminary photographic examination indicated the orthorhombic space group *Pbca*.[10a] On precession photographs of reciprocal lattice layers a^*b^* and b^*c^* there was a suggestion of diffuse scattering, in the form of slight, circular elongations of the reflections. The crystal density was

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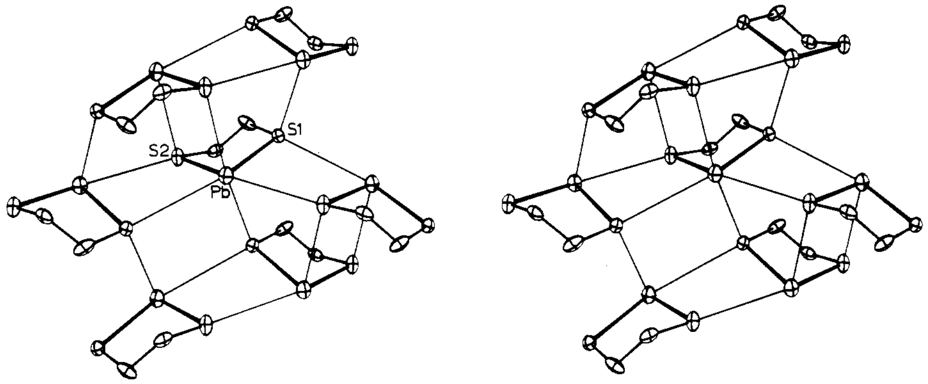

Figure 1. Stereoview of the "sheet" structure in the *ac* plane. The *c* axis is horizontal, and the *a* axis vertical.

measured with a Berman density balance, using toluene, at 23 °C.

The analysis was carried out on an Enraf-Nonius CAD4F diffractometer using an incident-beam monochromator and Mo radiation.[11] Preliminary cell constants and an orientation matrix were determined from reflections recorded on a rotation photograph and refined by using the optimized angular settings for 21 high-angle reflections with $30 < 2\theta < 39°$. ω-scans of intense, low-angle reflections had an average width at the base of 0.75°, a satisfactory value.[12] Crystal data are given in Table I. Intensity measurements were made at variable scan speeds ranging from 5.0 to 0.9° min^{-1}, values chosen to optimize counting statistics within a maximum time per datum of 90 s. Background estimates were made by extending the scan by 25% on each side.

Standard reflections 200, 020, 00$\bar{4}$, and 12$\bar{2}$ were monitored every 166 min of X-ray exposure time and showed an average 0.1% decay over the total period of 67.5 h. In all, 2383 observations were recorded, of which 120 were standards. Corrections were applied for Lorentz, monochromator and crystal polarization, and background radiation effects, by using the Structure Determination Package[13] running on a PDP 11/23+ computer. Standard deviations were assigned on the basis of counting statistics, and a starting value of 0.04 was chosen for p.[14] Ten crystal faces were identified by optical goniometry, and the crystal dimensions measured on a microscope equipped with a filar eyepiece. The data were corrected for absorption by the Gaussian method and the equivalent forms averaged ($R = 0.025$ on F_o for 104 pairs of reflections), leaving 2159 unique data of which only 1092 had $F_o > 3\sigma(F_o)$.

Solution and Refinement of the Structure

The structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares techniques on F. With all non-hydrogen atoms included, minimizing the function $\sum w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure amplitudes and the weight w is defined as $4F_o^2/\sigma^2(F_o^2)$, refinement converged at agreement factors $R_1 = \sum(||F_o| - |F_c||)/\sum(|F_o|) = 0.052$ and $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2} = 0.061$. Scattering factors for neutral, non-hydrogen atoms were taken from ref 10b, and real dispersion corrections were included for all atoms.[15] A difference Fourier synthesis showed clear evidence (peaks of 1.5 (7) – 1.7 (7) e·Å^{-3}) for all four H atoms, so all were included in idealized positions (C–H = 0.95 Å, sp^3 hybridization) with arbitrarily fixed isotropic thermal parameters. The H atom scattering factor values were taken from Stewart et al.[16] With all non-hydrogen atoms assigned anisotropic thermal parameters and H atom positions recalculated after each least-squares cycle to maintain ideal geometry, refinement converged at $R_1 = 0.051$ and $R_2 = 0.060$. An inspection of F_o and F_c suggested that an extinction parameter should be refined. Reflections 020 and 106 were assigned zero weights; then, employing a larger p factor of 0.07 and 1079 observations with $F_o > 3\sigma(F_o)$, refinement of 47 variables converged at agreement factors $R_1 = 0.040$ and $R_2 = 0.053$.

Table II. Atomic Positional (×10^4) and Thermal (×10^4) Parameters[a]

atom	x	y	z	U_{eq},[b] Å^2
Pb	2734.2 (7)	5341.1 (3)	1205.1 (4)	265.3 (8)
S(1)	4459 (4)	4174 (2)	2957 (3)	218 (6)
S(2)	3483 (5)	3925 (2)	−577 (3)	276 (7)
C(1)	5039 (16)	3144 (9)	1832 (14)	278 (27)
C(2)	3735 (16)	2928 (8)	680 (13)	232 (26)
H(1)	6173	3275	1421	84
H(2)	5126	2583	2402	84
H(3)	2596	2799	1083	84
H(4)	4141	2370	194	84

[a] H atom thermal parameters have been multiplied by 10^3. [b] $U_{eq} = {}^1/_3\sum_i\sum_j a_i{}^*a_j{}^*\mathbf{a}_i\mathbf{a}_j$.

In a final difference Fourier synthesis there were ten peaks with electron density greater than 1.3 (4) e·Å^{-3}, of which four were associated with the Pb atom at distances less than 0.80 Å, two were associated with S atoms at distances of 0.73 and 0.71 Å, and the other four peaks were around the Pb atom at distances 1.13 Å (1.8 (4) e·Å^{-3}), 3.52 Å (1.6 (4) e·Å^{-3}), 2.06 Å (1.5 (4) e·Å^{-3}), and 2.65 Å (1.4 (4) e·Å^{-3}). We then considered the possibility of disorder, remembering that some suggestion of this was noted on the precession photographs. A refinement using all 2159 unique data converged at $R_1 = 0.113$ and $R_2 = 0.075$ for 47 variables, with no significant differences from the original model. The 20 most intense peaks in a difference Fourier synthesis are listed in a supplementary table,[17] and of these only peaks 2, 5, 10, and 11 are found at distances greater than 2.5 Å from a Pb atom. Peaks 5 and 11 are close to S atoms (vide post). The remaining two peaks, 2 and 10, occur in positions that might correspond to C atoms in ethanedithiolate ligands forming bridges between two Pb atoms rather than a chelate ring to one Pb atom. However, the geometries of the resulting fragments were far from ideal (C–C bonds of 1.8 Å), and no satisfactory disorder scheme could be formulated. The majority of the remaining electron density is thus of no chemical significance, and though we note that there is possibly some disorder present, as suggested by the precession photographs, it is too slight to affect the validity of the model based upon 1079 observations with $F_o > 3\sigma(F_o)$, which is reported herein.

The error on an observation of unit weight was 1.02 electrons, and no shift exceeded 0.01σ in the final cycle. An analysis of R_2 in terms of F_o, $\lambda^{-1} \sin\theta$, and various combinations of Miller indices showed no unusual trends. The extinction parameter refined to 2.8 (1) × 10^{-7}. Positional and U(equivalent) thermal parameters for the refined structure are given in Table II. Tables of anisotropic thermal parameters, root-mean-square amplitudes of vibration, the weighted least-squares plane, torsion angles, difference Fourier peaks, and structure amplitudes have been deposited.[17]

Results and Discussion

In the solid state, **1** has a three-dimensional, thiolate-bridged polymeric structure, with the shortest nonbonded Pb··Pb distance being 4.202 (1) Å. The Pb atoms approach one another most closely within sheets extending in the direction of the *ac* plane, for there are six Pb··Pb nonbonded distances less than 5 Å within this plane. By contrast, the shortest Pb··Pb nonbonded distance perpendicular to the *ac* plane is 6.901 (1) Å. The polymeric sheet may be considered as a layer of Pb atoms sandwiched between layers of S atoms, with the periphery being formed by a hydrocarbon layer from the edt ligands. The shortest nonbonded interactions involving H atoms are 2.37 Å between H(2) and H(3)^b and 2.81 Å between H(1) and S(1)^b, distances comparable to the sum of the van der Waals radii. A stereoview of a segment of

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(17) Supplementary Material.

Table III. Bond Distances and Bond Angles for Pb(edt) (1)^{a,b}

atom 1	atom 2	dist, Å	atom 1	atom 2	dist, Å	atom 1	atom 2	dist, Å
Pb	S(1)	2.660 (3)	Pb	S(2)	2.655 (3)	S(1)	C(1)	1.836 (13)
Pb	S(1)^{c}	3.584 (3)	Pb	S(2)^{a}	3.056 (3)	S(2)	C(2)	1.838 (12)
Pb	S(1)^{b}	3.032 (3)	Pb	S(2)^{d}	3.376 (3)	C(1)	C(2)	1.503 (18)

atom 1	atom 2	atom 3	angle, deg	atom 1	atom 2	atom 3	angle, deg	atom 1	atom 2	atom 3	angle, deg
S(1)	Pb	S(1)^{c}	152.12 (6)	S(1)^{b}	Pb	S(2)^{a}	166.14 (8)	Pb^{b}	S(1)	C(1)	112.1 (4)
S(1)	Pb	S(1)^{b}	84.31 (7)	S(1)^{b}	Pb	S(2)^{d}	72.52 (8)	Pb	S(2)	Pb^{a}	94.5 (1)
S(1)	Pb	S(2)	82.0 (1)	S(2)	Pb	S(2)^{a}	85.5 (1)	Pb	S(2)	Pb^{c}	108.2 (1)
S(1)	Pb	S(2)^{a}	83.04 (9)	S(2)	Pb	S(2)^{d}	150.08 (6)	Pb	S(2)	C(2)	98.5 (4)
S(1)	Pb	S(2)^{d}	74.46 (9)	S(2)^{a}	Pb	S(2)^{d}	109.25 (9)	Pb^{a}	S(2)	Pb^{c}	88.17 (8)
S(1)^{c}	Pb	S(1)^{b}	87.84 (8)	Pb	S(1)	Pb^{d}	102.54 (9)	Pb^{a}	S(2)	C(2)	106.4 (4)
S(1)^{c}	Pb	S(2)	70.87 (8)	Pb	S(1)	Pb^{b}	103.7 (1)	Pb^{c}	S(2)	C(2)	148.5 (4)
S(1)^{c}	Pb	S(2)^{a}	100.81 (8)	Pb	S(1)	C(1)	102.1 (4)	S(1)	C(1)	C(2)	115.7 (8)
S(1)^{c}	Pb	S(2)^{d}	128.17 (8)	Pb^{d}	S(1)	Pb^{b}	92.16 (8)	S(2)	C(2)	C(1)	113.7 (8)
S(1)^{b}	Pb	S(2)	87.15 (9)	Pb^{d}	S(1)	C(1)	139.8 (4)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Symmetry codes: (a) $1 - x, 1 - y, -z$; (b) $0.5 + x, y, 0.5 - z$; (c) $0.5 - x, 1 - y, z - 0.5$; (d) $0.5 - x, 1 - y, 0.5 + z$.

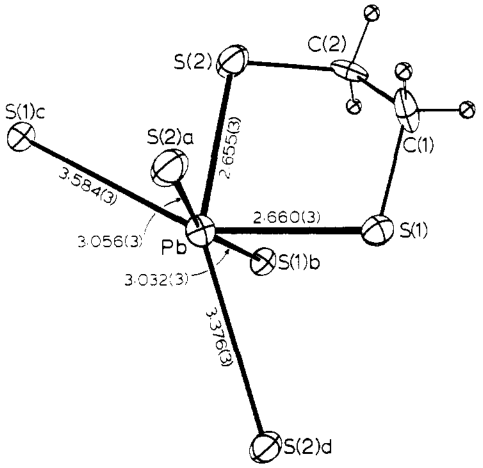

Figure 2. Perspective view of the Pb(edt) entity, showing the atom-numbering scheme and the immediate coordination sphere of the Pb atom. Atoms are drawn with 50% probability thermal ellipsoids.

the sheet is shown in Figure 1, viewed perpendicular to the *ac* plane. Intra- and intermolecular bond distances and bond angles are summarized in Table III.

Within the sheet structure of **1**, each Pb atom is bound to one chelating edt ligand, the sulfur atoms S(1) and S(2) of the chelate being strongly coordinated at 2.655 (3) and 2.660 (3) Å, respectively, so that Pb(edt) entities are recognizable. In addition, each Pb atom is associated with four further thiolate S atoms from four different neighboring Pb(edt) species (symmetry operations denoted by a, b, c, and d are given in Table III), at Pb–S distances of 3.032 (3), 3.056 (3), 3.376 (3), and 3.584 (3) Å, all less than the sum of the van der Waals radii, 3.8 Å.[18] The coordination geometry about the Pb atom in the PbS_6 kernel is that of a distorted octahedron, as shown in detail in Figure 2, with Pb–S distances ranging from 2.655 (3) to 3.584 (3) Å and S–Pb–S angles from 70.87 (8) to 128.17 (8)°. However, the combination of the large S(1)^{c}–Pb–S(2)^{d} angle of 128.17 (8)° and the long Pb–S(1)^{c} and Pb–S(2)^{d} interactions, 3.376 (3) and 3.584 (3) Å, respectively, raises the possibility that a stereochemically active lone pair of Pb electrons may be located between S(1)^{c} and S(2)^{d}. In this case the coordination geometry of lead would appear to be based on a pentagonal bipyramid, with the lone pair of electrons occupying an equatorial site, the kernel being of VSEPR type AX_6E.[19] (Alternative descriptions, depending on the significance attached to the various intermolecular interactions, would be that the Pb/S(1)/S(2) and Pb/S(1)/S(2)/S(1)^{b}/S(2)^{a} kernels are of the VSEPR types AX_2E and AX_4E, respectively.) In earlier studies, a similar pseudo-pentagonal-bipyramidal coordination of lead has been found in both lead(II) *O,O′*-diisopropyl phosphorodithioate (**2**)[20] and (D-penicillaminato)lead(II) (**3**).[21] The resemblance between the coordination spheres of lead in **1** and **2** is quite striking, while the results for **1** and **3** underscore the general structural complexity to be expected in the solid state for plumbous complexes of therapeutic chelators.

The shortest Pb–S distances in **1**, Pb–S(1) and Pb–S(2), are longer than the remarkably short terminal Pb–S distance of 2.554 (4) Å reported[2] for $[Pb(SAr')_2]_3$ (**4**).[22] They are, however, comparable to the values of 2.647 (1) and 2.646 (4) Å determined for the longest Pb–S bond of the discrete anion in $[Ph_4As][Pb(SPh)_3]$[5] and the shortest Pb–S distance of polymeric thiolate-bridged $Pb(mes)(NO_3)$,[3,23] respectively, though shorter than the intrachelate Pb–S distance of 2.716 Å measured[21] for **3**. Longer intrachelate distances have been reported for **2** and related species with four-membered chelate rings[20] (e.g. 2.761 (7) and 2.772 (7) Å for **3**); in this case the longer distances are perhaps attributable to the greater strain associated with the smaller chelate rings. The longest intermolecular Pb⋯S interaction in **1**, Pb–S(1)^{c} = 3.584 (3) Å, is comparable to an intermolecular Pb⋯S distance of 3.55 Å given in a preliminary report[24] of the chain structure of the chelate $Ph_2Pb(edt)$, while the 82.0 (1)° bite angle of the chelating edt ligand in **1** is at the lower end of the range of 80.97 (9)–93.1° reported for other complexes.[25]

In the five-membered chelate rings of the Pb(edt) molecules, C(1) and C(2) are displaced by 0.02(1) and 0.73 (1) Å, respectively, from the plane formed by the Pb and two S atoms, giving rise to a pseudo-envelope conformation. As a result of the intermolecular interactions, each of the two crystallographically distinct S atoms is surrounded by three Pb atoms and the attached C atom in a distorted tetrahedral arrangement, Figure 1. At S(1), the angles range from 92.16 (8) to 139.8 (4)°, while for S(2) the range is from 88.17 (8) to 148.5 (4)°. The μ_3-sulfur atoms and extensive polymerization occurring in **1** can be contrasted with

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the occurrence of only terminal and μ_2-sulfur atoms in the trimer **4**.[3] The difference is readily attributed to the much smaller steric bulk of the edt ligand.

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Registry No. 1, 86860-88-0.

Supplementary Material Available: Listings of anisotropic thermal parameters, root-mean-square amplitudes of vibration, torsion angles, the weighted least-squares plane, difference Fourier peaks, and structure amplitudes (14 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Gorlaeus Laboratories,
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Linear Trinuclear Transition-Metal Compounds Containing 3,5-Diethyl-1,2,4-triazole and Fluoride as Bridging Ligands. X-ray Structure of Bis[(μ-fluoro)bis(μ-3,5-diethyl-1,2,4-triazole-N^1,N^2)bis(thiocyanato-N)(3,5-diethyl-1,2,4-triazole-N^1)cobalt(II)-F,N^1,$N^{1'}$]cobalt(II) Dihydrate

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The synthesis and characterization of three isomorphous trimers containing 3,5-diethyl-1,2,4-triazole are described. The compounds are of general composition $[M_3(detrH)_6(NCS)_4F_2](H_2O)_2$ (M = Mn, Co, Ni). A single-crystal X-ray analysis of the Co compound shows the presence of a linear trinuclear unit $(SCN)_2(detrH)Co(detrH)_2FCoF(detrH)_2Co(detrH)(NCS)_2$. This compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.251$ (2) Å, $b = 20.899$ (3) Å, $c = 17.320$ (4) Å, $\beta = 101.57$ (2)°, and $Z = 2$. The structure was solved by using standard heavy-atom techniques and a local set of programs for automatic crystal structure determination. Conventional least-squares refinement techniques resulted in final residuals $R = 0.032$ and $R_w = 0.043$. Neighboring Co(II) ions in the linear centrosymmetric trinuclear species are linked by two 1,2-bidentate triazole ligands and one bridging fluoride anion. The coordination sphere of the terminal Co(II) ions is completed by two N-bonded thiocyanate anions and one monodentate triazole ligand. The Co···Co distance in the trimer is 3.3726 (3) Å. The Co–F distances are 1.992 (1) and 2.019 (1) Å. The Co–N distances are in the range 2.09–2.21 Å. Fitting of the magnetic data of the Ni trimer according to the isotropic Heisenberg model results in $J = -11.1$ (9) cm^{-1} ($J/k = -16.0$ K) and $g = 2.28$ (1). An expression for the susceptibility of the Co trimer according to the Ising model is derived by assuming an effective spin of $^1/_2$ for Co and neglecting $\chi_\perp$. Fitting of the magnetic data of the Co compound to the expression obtained yields $J_\parallel = -17.4$ (7) cm^{-1} and $g_\parallel = 8.23$ (4). The magnetic properties of the fluoride-bridged trimers are compared to magnetic data of closely related compounds containing N-bridging isothiocyanato ligands instead of fluoride anions.

Introduction

Current research activity concerning the structural and magnetic properties of polynuclear transition-metal compounds is aimed at understanding the structural and chemical features governing magnetic exchange coupling through small bridging ligands. The literature on this subject is exhaustive, mainly dealing with dimeric compounds[1-6] and chains.[7-9] Linear trinuclear compounds for which structural *and* magnetic information is available are documented to a limited extent.[10-15] Recently it was reported[16] linear trinuclear compounds are formed when transition-metal thiocyanates are reacted with 3,5-dialkyl-1,2,4-triazoles; neighboring metal ions (Co, Mn, Ni) in the linear array are linked by two 1,2-bidentate triazole ligands and one N-bridging isothiocyanato ligand. It was suggested that the double-triazole-bridging framework should also allow incorporation of anions other than thiocyanate, e.g., fluoride or hydroxide: such changes are interesting because changing the bridging anion might be a powerful tool in tuning the magnetic properties of these systems. The crystal structure now reported of $[Co_3F_2(detrH)_6(NCS)_4](H_2O)_2$ proves that incorporation of fluoride anion is possible; moreover, magnetic susceptibility data of both the Ni and the Co trimers in the 4–80 K region reveal quite substantial differences between the exchange constants of the fluoride-bridged and isothiocyanate-bridged compounds. In the present study we try to account for these differences in a qualitative way by comparison of the M–X–M

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