Thiolate Coordination in Binuclear and Tetranuclear Oxomolybdenum Complexes: Syntheses and Crystal Structures of Diammonium Bis{μ-[(mercapto-κS:κS)acetato(2−)-κO]}bis[(mercapto-κS)acetato(2−)-κO]dioxodimolybdate(2−)(*Mo−Mo*) ($(NH_4)_2[Mo_2O_2(SCH_2COO)_4]$) and Ammonium Trisodium Hexakis{μ-[(mercapto-κS:κS)acetato(2−)-κO]}bis[(mercapto-κS)acetato(2−)-κO]dioxotetramolybdate(4−)(3*Mo−Mo*) Decahydrate ($(NH_4)Na_3[Mo_4O_2(SCH_2COO)_8] \cdot 10\ H_2O$)

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The reaction of $Na_2MoO_4 \cdot 2\ H_2O$ with mercaptoacetic acid and NH_4Cl in H_2O yielded a new complex, $(NH_4)_2[Mo_2O_2(\mu\text{-}SCH_2COO)_2(SCH_2COO)_2]$ (**1**). Complex **1** exhibits a bi-octahedral geometry similar to that reported for $(Bu_4N)_2[Mo_2O_2(SCH_2COO)_4]$, but the former is connected *via* S−S interactions to a chain, and then linked to a three-dimensional framework *via* H-bonds with $d(N \cdots O) = 2.791 - 2.887$ Å and $<(N-H \cdots O) = 147 - 166°$. Using a similar reaction system but, additionally, adding the strong reducing reagent $NH_2NH_2 \cdot 2\ HCl$, we have now succeeded in isolating a novel tetranuclear mixed-valence complex $(NH_4)Na_3[Mo_4O_2(\mu\text{-}SCH_2COO)_6(SCH_2COO)_2] \cdot 10\ H_2O$ (**2**), representing the first example of a new class of tetranuclear Mo−S complexes with a linear metal−metal chain. The ^{95}Mo-NMR spectrum of **2** exhibits two single peaks at δ 1722.9 and 942.7, attributed to Mo^{V} and Mo^{III}, respectively. ^{13}C- and ^{1}H-NMR and magnetic studies are discussed in detail. Crystallographic data of **1**: monoclinic space group $P2(1)/n$, $a = 11.7595(4)$, $b = 5.8320(10)$, $c = 13.9728$ Å, $\beta = 96.587(2)°$, $V = 951.95(5)$ Å^3, $Z = 2$, $R = 0.0378$, and *g.o.f.* = 1.106; data of **2**: triclinic space group $P(-1)$, $a = 12.7873(2)$, $b = 14.05640(10)$, $c = 15.0112(2)$ Å, $\alpha = 109.4710(10)$, $\beta = 110.6020(10)$, $\gamma = 101.6020(10)°$, $V = 2220.79(5)$ Å^3, $Z = 2$, $R = 0.0400$, and g.o.f. = 1.064.

Introduction. – In recent decades, great efforts have been made to study thiolatomolybdenum cluster complexes because of their unusual catalytic activities in biological and industrial processes [1], and their intriguing optical and electrical properties [2]. These efforts have resulted in the discovery of numerous polynuclear Mo and Mo-heterometallic complexes bearing metal−metal bonds [3]. Of these polynuclear cluster complexes, the most interesting one is the tetranuclear family. Among the reported tetranuclear complexes, almost all display M−M bonded arrangements in a planar rhombus/rectangle/square [4], nonplanar butterfly [5], or tetrahedral framework [6]; only a few molybdenum-containing tetranuclear clusters exhibit linear arrangements, such as $[Mo_4(\mu_3\text{-}N)_2(\mu_2\text{-}{}^iPrO)_2({}^iPrO)_{10}]$ [7], $[Mo_2Pd_2Cl_2(pyphos)_4]$ (pyphos = 6-(diphenylphosphino)pyridin-2(1*H*)-onato) [8], $[Mo_2M_2X_4(pyphos)_4]$ (X = Cl, Br, I, M = Pd, Pt) [9], and $[Me_3N(CH_2Ph)]_2[NH_4]_2[Fe_2S_2(MoS_4)_2]$ [10]. Many M_2 complexes with multi M−M bonds may undergo an interesting addition reaction, providing a valuable synthetic route to the metal chains [9]; however, the studies of tri-, tetra-, and higher multinuclear cluster with an M−M-bonded linear chain are still in an embryonic state [7–13]. Using $Na_2MoO_4 \cdot 2\,H_2O$, mercaptoacetic acid (=thioglycolic acid; $HSCH_2COOH$), and NH_4Cl as starting materials, we have now succeeded in isolating a new dinuclear mercaptocarboxylato(2–) complex $(NH_4)_2[Mo_2O_2(\mu\text{-}SCH_2COO)_2(SCH_2COO)_2]$ (**1**), which was further reduced to a novel tetranuclear mixed-valence complex $(NH_4)Na_3[Mo_4O_2(\mu\text{-}SCH_2COO)_6(SCH_2COO)_2] \cdot 10\,H_2O$ (**2**). Compound **2** was found to be the first tetranuclear Mo–S cluster complex containing a $Mo_4(\mu_2\text{-}S)_6$ core with a linear Mo–Mo–Mo–Mo chain. Here, we report the synthesis and structural characterization of **1** and **2**.

Results and Discussion. – *Synthesis.* It was reported that, when molybdate(VI) was treated with excess mercaptoacetic acid ($HSCH_2COOH$), 'dimerization' occurred to afford several dinuclear oxo(thiolato)molybdenum(V) complexes [14] (*Eqns. 2* and *3*). These dinuclear complexes were proposed to be formed *via* a $Mo^{VI} \rightarrow Mo^{IV} \rightarrow Mo^{V}_2$ mechanism, which involves the formation of the bis[mercaptocarboxylato(2–)]dioxomolybdenum complex $[Mo^{VI}O_2(SCH_2CO_2)_2]^{2-}$ (*cf. Eqn. 1*) that is subsequently reduced by excess of $HSCH_2COOH$ to give an intermediate mononuclear Mo^{IV} species (*Eqn. 4*), and then 'dimerizes' rapidly with $[Mo^{VI}O_2(SCH_2CO_2)_2]^{2-}$ to give Mo^{V}_2 complexes (*Eqn. 5*). When the sterically encumbered bis[mercaptocarboxylato(2–)]dioxomolybdenum complexes are reduced, the formation of mononuclear $Mo^{V}O$ complexes occurs through reactions as shown in *Eqns. 4* and *5* [14]. Based on this finding, reaction of $(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O/NaOH$ in H_2O with an excess of $HSCH_2COOH$ in the presence of a high concentration of electrolyte NH_4Cl (1.5M) resulted in a new dinuclear dioxomolybdenum(V) complex $(NH_4)_2[Mo^{V}_2O_2(SCH_2COO)_4]$ (**1**). Furthermore, when **1** in H_2O was treated with $NH_2NH_2 \cdot 2\,HCl$ and NaCl, a novel air-stable tetranuclear Mo^{V}/Mo^{III} mixed-valence mercaptocarboxylato(2–) complex $(NH_4)Na_3[Mo_4O_2(\mu\text{-}SCH_2COO)_6(SCH_2COO)_2] \cdot 10\,H_2O$ (**2**) with a linear metal chain was isolated. In fact, compound **2** was also obtained directly by a similar reaction in H_2O only in the presence of $NH_2NH_2 \cdot 2\,HCl$. The formation of **1** and **2**, as well as previous investigations, suggest that the Mo^{V}_2 complex in solution can be further reduced to Mo^{III}_2 intermediates containing a Mo–Mo multiple bond, and then rapidly 'dimerize' with the Mo^{V} species of the reaction of *Eqn. 5*, giving the mixed-valence complex **2** *via* the reaction of *Eqn. 6*.

$$MoO_4^{2-} + HSCH_2COOH \xrightarrow{Bu_4NBr} [Mo^{VI}O_2(SCH_2CO_2)_2]^{2-} \qquad (1)$$

$$Mo_8O_{26}^{4-} + HSCH_2COOH \xrightarrow{EtN} [Mo^{V}_2O_2(SCH_2CO_2)_4]^{2-} \qquad (2)$$

$$MoO_4^{2-} + HSCH_2COOH \xrightarrow[2)\ Bu_4NBr]{1)\ pH\,5.0} [Mo^{V}_2O_3(SCH_2CO_2)_3]^{2-} \qquad (3)$$

$$MoO_4^{2-} + HSCH_2CO_2H \rightarrow$$
$$Mo^{VI}O_2(SCH_2CO_2)_2]^{2-} \xrightarrow{\text{excess } HSCH_2CO_2H} [Mo^{IV}O(SCH_2CO_2)_2]^{2-} \qquad (4)$$

$$[Mo^{VI}O_2(SCH_2CO_2)_2]^{2-} + [Mo^{IV}O(SCH_2CO_2)_2]^{2-} \rightarrow$$
$$[Mo^{V}_2O_3(SCH_2CO_2)_4]^{4-} \xrightarrow[-H_2O]{2\,H^+} 2[Mo^{V}O(SCH_2CO_2)_2]^{-} \qquad (5)$$

$$[\mathrm{Mo^{V}_2O_2(SCH_2CO_2)_4}]^{2-} \xrightarrow{\mathrm{NH_2NH_2\cdot 2HCl}} [\mathrm{Mo^{III}_2O_2(SCH_2CO_2)_4}]^{6-} \xrightarrow[-2\mathrm{H_2O}]{2[\mathrm{Mo^{V}O(SCH_2CO_2)_2}]^{-}+4\mathrm{H}^{+}}$$

$$[\mathrm{Mo^{V}_2Mo^{III}_2O_2(SCH_2CO_2)_8}]^{4-} \tag{6}$$

Structural Features. As shown in *Fig. 1,a*, the anion structure of **1** consists of a dinuclear species $[\mathrm{Mo^{V}_2O_2}(\mu\text{-}\mathrm{SCH_2CO_2})_2(\mathrm{SCH_2CO_2})_2]^{2-}$ whose skeleton is very similar to that reported for $(\mathrm{Bu_4N})_2[\mathrm{Mo_2O_2(SCH_2COO)_4}]$ [14a], with a crystallographic center of symmetry at the midpoint of the Mo(1)–Mo(1A) vector. The mercaptoacetato(2 –) ligands display two distinct coordination modes: the terminal mode involves chelating through S(2) and O(3), and the bridge mode involves chelating of S(1) by bridging two Mo-atoms while O(1) is bonded to a single Mo-site. The two distinct mercaptoacetato(2 –) ligands are essentially planar and nearly perpendicular to each other with a dihedral angle of 86.3°.

Complex **1** is characterized by the crystallographic planarity of a $\mathrm{Mo_2S_2}$ rhombus and a '*trans*'-position of two terminal atoms. The Mo(1)–Mo(1A) distance of 3.0272(9) Å is notably longer than those generally observed for dinuclear molybdenum(V) complexes with two Mo-atoms sharing a face or bridge. Another important structural feature is that the molecular anions are first connected *via* S–S interactions (S(1) ··· S(1′) distances 3.51 Å) into a chain (see *Fig. 1,b*), which is further linked to a three-dimensional framework *via* H-bonds (see *Fig. 1,c*), each $\mathrm{NH_4}^+$ cation exhibiting four H-bonds with the O-atoms donated from the mercaptoacetato(2 –) ligands (d(N ··· O) = 2.791-2.884 Å and < (N–H ··· O) = 148–170°).

The X-ray analysis revealed that the crystal structure of **2** is constructed from tetranuclear molybdenum complex anions $[\mathrm{Mo_4O_2}(\mu\text{-}\mathrm{SCH_2COO})_6(\mathrm{SCH_2COO})_2]^{4-}$ (**2a**) linked through $\mathrm{Na^+}$ cations (Na–O bonds: 2.312–2.527 Å; Na–$\mathrm{OH_2}$: 2.332–2.685 Å) and H-bonds (d(N ··· O) = 2.836–2.889 Å and d(O ··· O) = 2.723–2.878 Å) into a three-dimensional framework. As shown in *Fig. 2*, each tetranuclear anion contains a tortuous linear $\mathrm{Mo_4}(\mu_2\text{-S})_6$ bridge, the angle Mo(3)–Mo(2)–Mo(1) being 117.37(2)° and that of Mo(2)–Mo(3)–Mo(4) being 116.00(2)°, where the μ_2-S atoms derive from a fully deprotonated mercaptoacetato(2 –) ligand. Each terminal Mo-atom (Mo(1) and Mo(4)) is bonded to a terminal oxo ligand and one terminal didentate mercaptoacetato(2 –) ligand acting through the S-atom and a carboxylic O-atom; the octahedral coordination of Mo(1) or Mo(4) is completed by two μ_2-S moieties from the bridging mercaptoacetato(2 –) ligands. Mo(2) or Mo(3) is coordinated to four mercaptoacetato(2 –) ligands through their carboxylic O-atom and thiolic bridging S-atom. There are two short Mo–O bonds of *ca.* 1.68 Å and eight longer Mo–O bonds of *ca.* 2.06–2.17 Å, formally corresponding to Mo–O double and single bonds, respectively. The Mo–S distances (2.386–2.481 Å) observed in **2a** are clearly in the range observed for formal Mo–S single bonds (*ca.* 2.23–2.55 Å [15]).

Alternatively, the tetranuclear complex anion **2a** can be regarded as two dinuclear $[\mathrm{Mo}(\mu\text{-}\mathrm{SCH_2COO})_2(\mathrm{SCH_2COO})\mathrm{MoO}]$ moieties linked to each other through a mercaptoacetato(2 –)-supported metal–metal bond (2.76 Å). The two dinuclear moieties show an unusual boat conformation for $\mathrm{Mo}(\mu\text{-}\mathrm{SCH_2COO})_2\mathrm{Mo}$ with a Mo–Mo bond length of *ca.* 2.98 Å and the μ-$\mathrm{SCH_2COO}$ ligands coordinated to the Mo-atoms in '*cis*'-position. This coordination type is very different from that found in

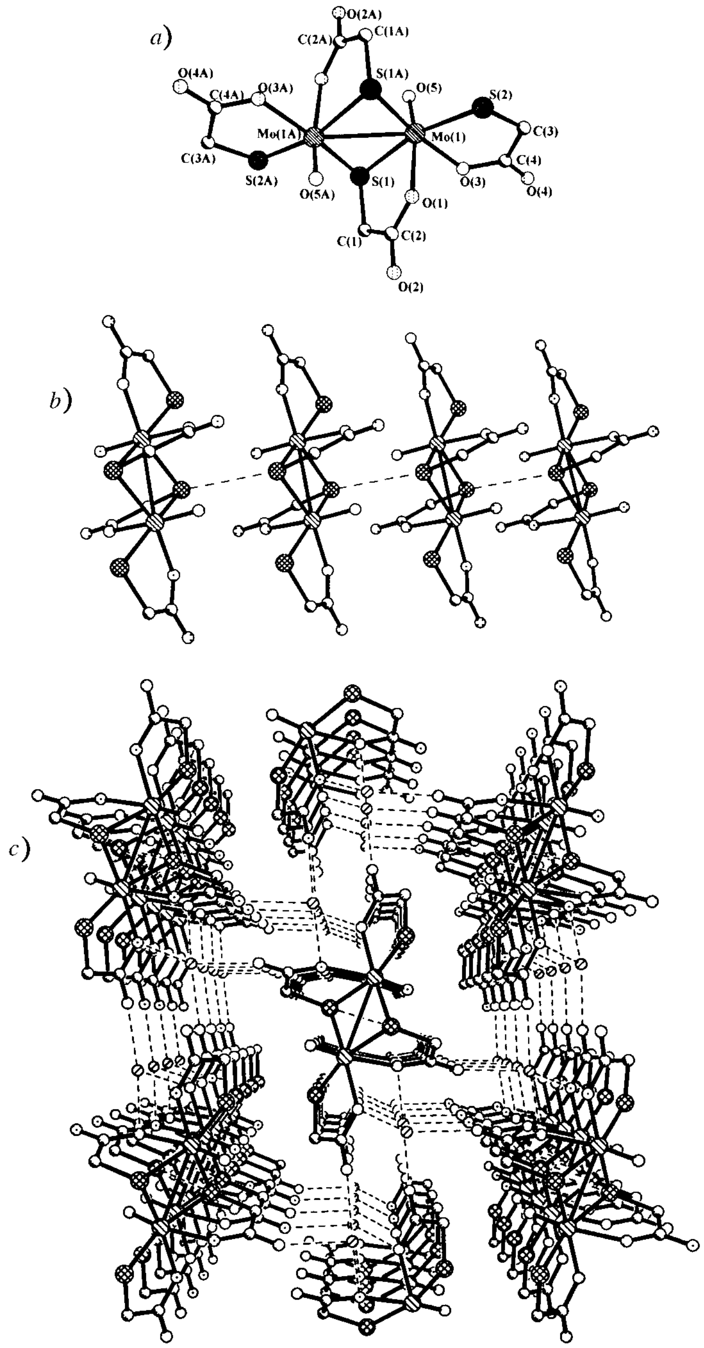

Fig. 1. a) *Structure of anion* $[Mo_2O_2(SCH_2CO_2)_4]^{2-}$, b) *linkage of the* $[Mo_2O_2(SCH_2CO_2)_4]^{2-}$ *anions* via *S* ··· *S interactions* (S(1) ··· S(1), 3.510(3) Å) *into a chain, and* c) *connection into a three-dimensional framework* via *H-bonds.* All H-atoms are omitted for clarity.

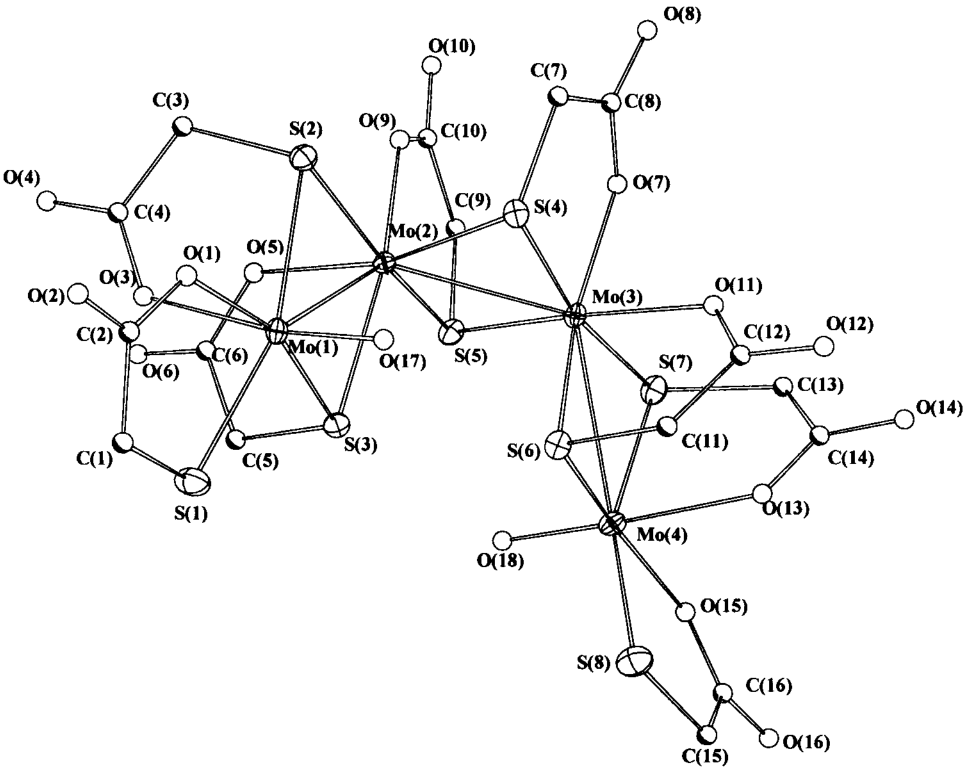

Fig. 2. *Structure of anion* $[Mo_4O_2(\mu\text{-}SCH_2CO_2)_6(SCH_2CO_2)_2]^{4-}$ (**2a**) *with atom labeling*

other dinuclear (mercaptocarboxylato)molybdenum complexes [14]. Interestingly, in each $Mo(\mu\text{-}SCH_2COO)_2Mo$ moiety, the two bridging mercaptoacetato(2 –) ligands are essentially planar, almost parallel to each other (dihedral angles $12 \pm 1°$), and approximately perpendicular to the Mo–S coordination plane defined by the corresponding $Mo_2(\mu\text{-}S)_2$ ring (dihedral angles within 84–94°). Moreover, the two dinuclear moieties are arranged in a nonplanar '/ \' conformation (the dihedral angle between two $Mo_2(\mu\text{-}S)_2$ rings is 11.2°), which allows two additional bridging mercaptoacetato(2 –) ligands to coordinate to two central Mo-atoms also in '*cis*'-positions, forming the short Mo(2)–Mo(3) bond (2.76 Å).

Bonding Considerations and Magnetic Susceptibility Measurements. In anion **2a**, four molybdenum ions contribute a total of eight valence electrons for metal–metal bonding. The Mo–Mo distances, two long ones of 2.98 Å (average) and a short one of 2.76 Å, suggest that two Mo^V units are attached to a $(Mo_2)^{6+}$ center. The value of the short distance Mo(2)–Mo(3) (2.76 Å; corresponding Mo–S–Mo angles, 69.80 and 69.89°) is borderline between the M–M double-bond distances (2.68–2.77 Å; corresponding Mo–S–Mo angles, 67.9–70.0°) as found in $[Mo^{III}Cl_2(LL)(\mu\text{-}SPr)]_2$ (Pr = propyl, LL = $PrSCH_2CH_2SPr$ and $Et_2PCH_2CH_2PEt_2$) with planar $Mo_2(\mu\text{-}S)_2$ rings [16], and the M–M single-bond distances (2.77–2.83 Å; corresponding Mo–S–Mo angles, 72.9–75.6°) as found in $[Mo_2O_2(\mu\text{-}S)_2L_2]$ (L = bidentate sulfido ligands) [17]. The value of the long distances (2.98 Å (average)) is close to those of typical M–M single bonds. Based on bond-distance considerations, one could reasonably conclude that complex **2** may be paramagnetic. Indeed, the powder ESR spectrum of **2** at room temperature exhibits a paramagnetic center ($g = 1.9939$ and $A = 30.33$ G, which are close to the values found for $[Mo_2(3,5\text{-}Me_2C_6H_3O)_4]^+$ [18]) with six hyperfine lines. Temperature-dependent magnetic-susceptibility measurements were performed in the range of 4–300 K. As shown in *Fig. 3*, solid-state magnetic measurements indicated that in the temperature range 250–300 K, magnetic moments of *ca.* 1.0 μ_B were observed which decreased with decreasing temperature (0.19 μ_B at 5 K), indicating strong antiferromagnetic coupling (*Fig. 3,b*). Similar magnetic behaviors have been found for many multiply bonded Mo_2 compounds such as $Mo_3Cl_9^{3-}$ salts [19], $(Bu_4N)_2Mo_2Cl_9$ [19], and $[Me_2NH_2][Mo_2(4\text{-}MeC_6H_4O)_7(Me_2NH)_2]$ [18].

Spectroscopic Characterization. The IR and *Raman* spectra of **2** exhibit the vibration band $\tilde{\nu}$(Mo=O) at 933 and 937 cm^{-1}, respectively, and bands in the range 1000–1610 cm^{-1} characteristic of $[SCH_2COO]^{2-}$ dianions. In addition, the $\tilde{\nu}$(Mo–Mo) band appears at 189–216 cm^{-1}, in accordance with the value observed by *Saito et al.* (170–200 cm^{-1}) [20]. The absorption band at 3435 cm^{-1} is consistent with the presence of crystallization water in the structure. The UV/VIS spectrum of **2** exhibis maxima at 225 and 380 nm, respectively. The intense band at 225 nm is characteristic for a $n \rightarrow \pi^*$ transfer of the coordinated ligands, while the absorption at 380 nm should be assigned to a ligand-to-metal charge-transfer band.

The ^{13}C- and ^{1}H-NMR spectra of **2** show a complicated series of signals corresponding to the bound mercaptoacetato(2–)-ligands. In the carboxy region, there are four ^{13}C-NMR signals at 188.0, 181.6, 180.8, and 177.9 ppm, whereas in the CH_2 region four resonances at 50.6, 40.7, 37.5, and 32.8 ppm appear, indicating the presence of four different coordination environments for the mercaptoacetato(2–) ligands (*Fig. 4,a*). However, two pairs of chemical shifts are very close to each other (181.6 and 180.8, and 40.7 and 37.5), suggesting similarity between corresponding ligand environments.

The ^{1}H-NMR spectrum (*Fig. 4,b*) reveals three four-line *AB* patterns associated with the CH_2 groups of the mercaptoacetato(2–)-ligands. This indicates that complex **2** contains three distinct ligand environments, which seems to be inconsistent with the conclusion derived from the ^{13}C-NMR spectrum. In fact, two of the four four-line *AB* patterns arising from four different ligand environments are too close to be distinguished, and the observed integration of the *AB* spin systems reveals indeed a ratio of 1:2:1. Thus, the ^{13}C- and ^{1}H-NMR results suggest the presence of an approximate C_2 axis of symmetry in **2**, which leads to four different, distinct ligand environments for the coordinated mercaptoacetato(2–) ligands.

^{95}Mo-NMR is a useful technique for the study of molybdenum compounds; however, observation of ^{95}Mo-NMR signals relies on various factors. Mononuclear Mo^{V} and Mo^{III} complexes have a d^1 or d^3 electron configuration exhibiting paramagnetism and are, therefore, not readily amenable to ^{95}Mo-resonance studies [21]. To date, most of the Mo^{V} and Mo^{III} complexes studied by ^{95}Mo-NMR are diamagnetic dinuclear species featuring a δ bond or a metal–metal triple bond. The observation of ^{95}Mo-NMR signals for trinuclear, tetrahedral, or bridged molybdenum compounds has

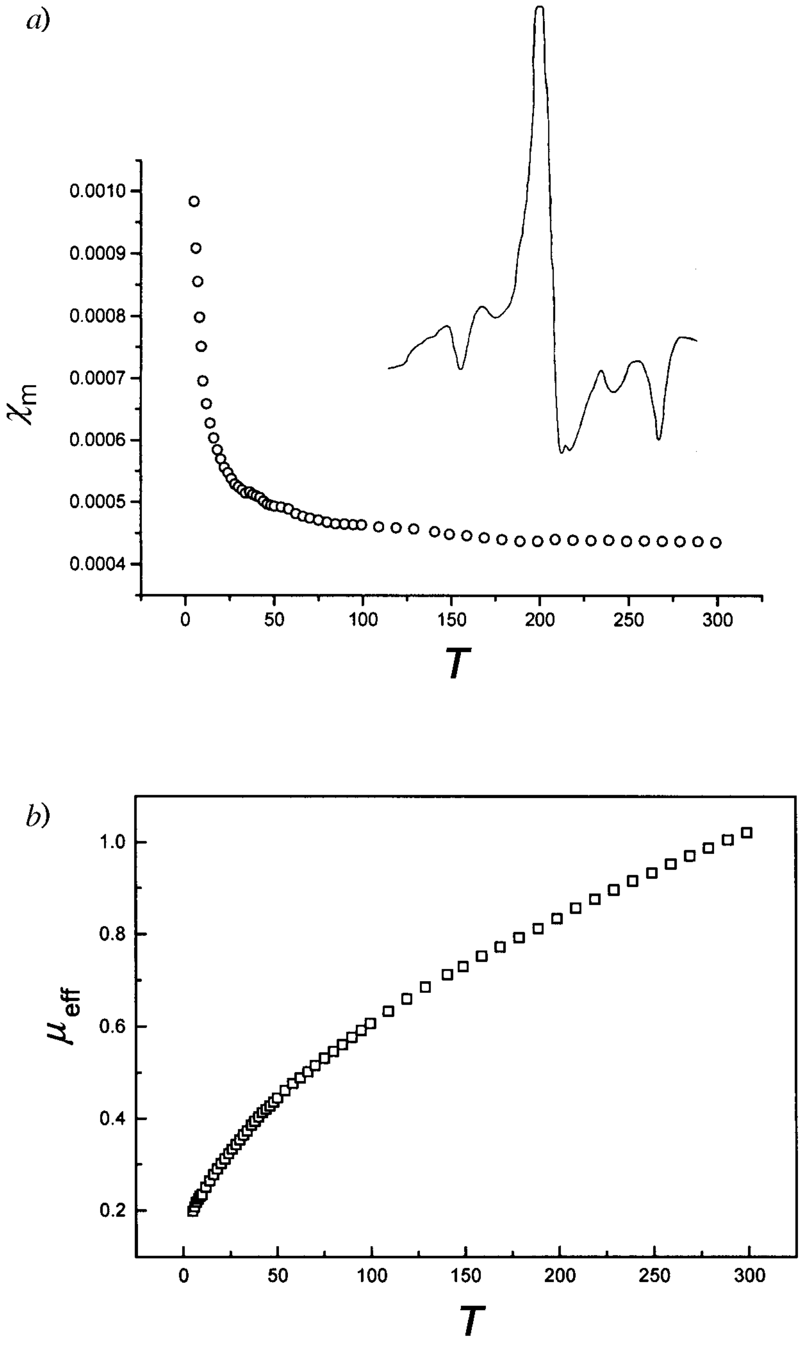

Fig. 3. *Temperature dependence of* a) χ_m *and* b) μ_{eff} *for* **2**. Insert: *ESR spectrum of* **2**.

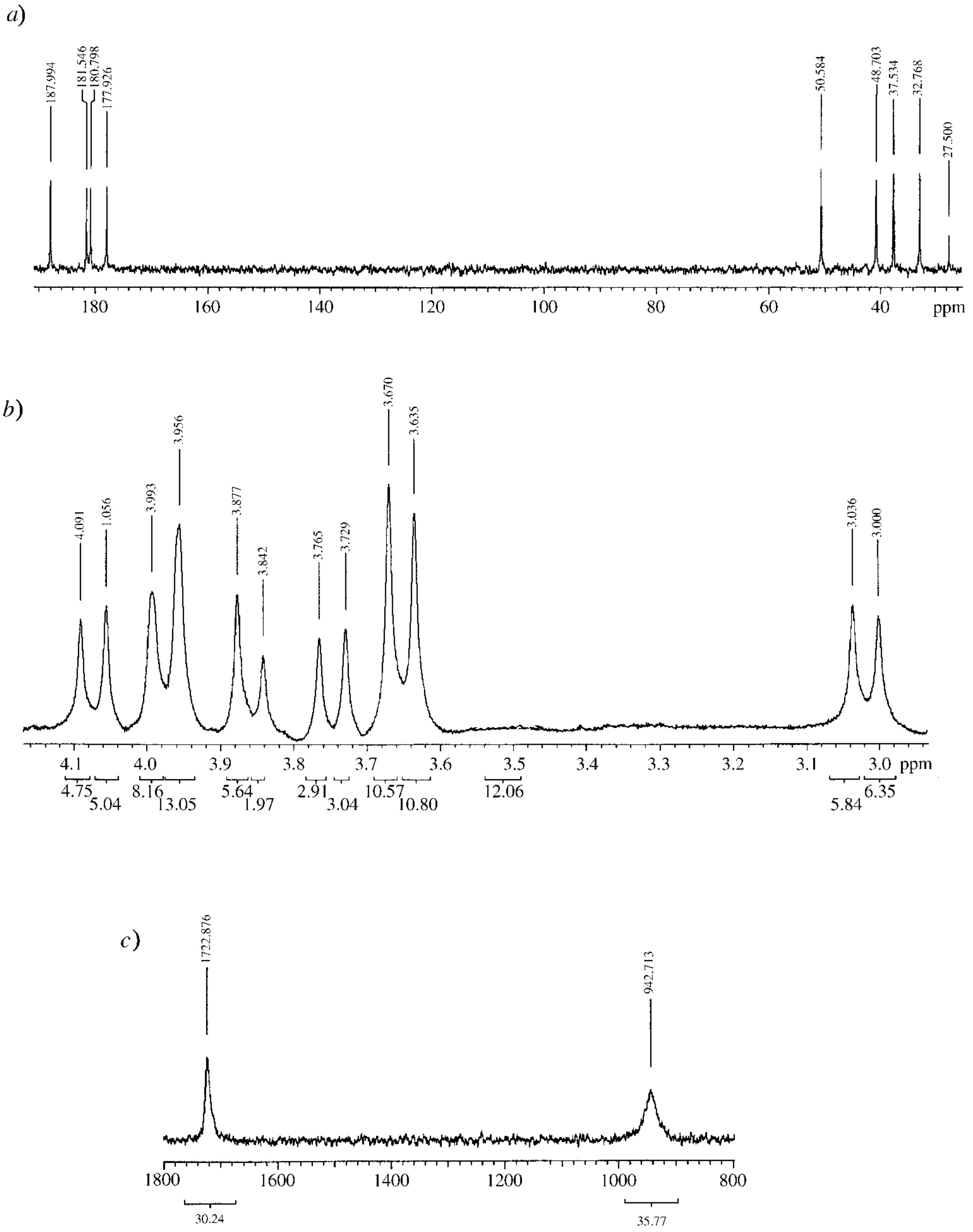

Fig. 4. a) *^{13}C-NMR,* b) *^{1}H-NMR, and* c) *^{95}Mo-NMR spectra of* **2** *in D_2O*

been difficult due to the usually low solubility or the short relaxation time. However, a D_2O solution of the tetranuclear mixed-valence complex **2** was found to be rather stable for extended periods of time, and unchanged spectra were obtained after an interval of a week. As shown in *Fig. 4,c*, complex **2** presents two single peaks in an intensity ratio of 1:1 at δ 1722.9 and 942.7 ppm, and the corresponding line widths are 110 and 696 Hz, respectively. Two different explanations can be proposed to account for the ^{95}Mo-NMR results. In the first explanation, all Mo-atoms are assumed to be in the oxidation state IV. The observation of two ^{95}Mo-signals would then arise from the presence of two different types of coordination of the Mo by the mercaptoacetato(2 –) ligands and terminal oxo ligands. This is consistent with the structural analysis. Generally, the electron density and magnetic shielding of the Mo-atoms increase as the metal–metal interactions increase, causing a shift of the ^{95}Mo-signal to the high-field region [15]. According to this effect, the peak at higher field (942.7 ppm) is assigned to Mo(2) and Mo(3), while the peak at 1722.9 ppm is attributed to the Mo(1) and Mo(4) centers.

But from the dependence of the chemical shift upon the oxidation state [21], and from the above-mentioned ESR spectrum and magnetic-susceptibility measurement of **2**, the second explanation seems to be more reasonable; *i.e.*, the observation of two separate ^{95}Mo-signals in an intensity ratio of 1:1 indicates valence trapping of $Mo^{V}_2Mo^{III}_2$, with the signal at lower field (1722.9 ppm) arising from the terminal $^{95}Mo^{V}$ atoms, and the peak at 942.7 ppm arising from the $^{95}Mo^{III}$ atoms (Mo(2) and (Mo(3)).

Conclusions. – Although previous studies in 1966 showed that the reduction of an aqueous molybdate solution by mercaptoacetic acid yielded a paramagnetic solution [22], subsequent attempts to isolate molybdenum-cluster complexes containing mercaptoacetic acid or its derivatives have been unsuccessful; to date, only few mononuclear Mo^{IV} and dinuclear Mo^{V} products have been isolated [23]. To the best of our knowledge, molybdenum-containing tetranuclear clusters with a linear arrangement of the four Mo-atoms are rather rare in the literature [7–14]. Although the structure of **1** is similar to that of $(Bu_4N)_2[Mo_2O_2(SCH_2COO)_4]$ [14a], complex **2** represents the first tetranuclear thiolato cluster complex containing a $Mo_4(\mu_2\text{-}S)_6$ core with a linear Mo–Mo–Mo–Mo chain, and another example of a linear Mo_4 structural type was previously only observed in $[Mo_4(\mu_3\text{-}N)_2(\mu_2\text{-}^iPrO)_2(^iPrO)_{10}]$ [7]. The cluster core of **2** can be regarded as a fusion of two planar $Mo_2(\mu_2\text{-}S)_2$ rings, which have been extensively reported [24]. Two fused $Mo_2(\mu_2\text{-}S)_2$ rings are linked together by two bridging thiolato donors (S(4) and S(5)), besides by the direct metal–metal bonding. Complex **2** exhibits paramagnetic features at room temperature with strong antiferromagnetic coupling. Attempts to isolate other tetranuclear or higher-multinuclear metal complexes with a linear metal chain are under way.

Experimental Part

General. All reactions were carried out in air. Reagents were purchased from *Aldrich Chemical Co.* and used without further purification. UV/VIS Spectra: *Cary UV-2390* instrument; H_2O as solvent; λ_{max} in nm, ε in M^{-1} cm^{-1}. IR and *Raman* ($\lambda = 1064$ nm) Spectra: *Nicolet Magna-750FT-IR* spectrometer; KBr pellet and KBr diluted, resp.; in cm^{-1}. ESR Spectra: *Bruker ESR-420* spectrometer (X-band). NMR Spectra: *Varian Unity-500* spectrometer; at 499.849, 125.704, and 32.494 MHz for ^{1}H,^{13}C, and ^{95}Mo, resp.; D_2O solns.; chemical shifts δ rel.

to cyclohexane (δ 27.5) and Na_2MoO_4 as ^{13}C and ^{95}Mo external reference standard, resp., and rel. to DSS ($Me_3Si(CH_2)_3SO_3Na$) as ^1H internal reference. The elemental analyses of C, H, and S were performed on an *EA1110-CHNS-0-CE* elemental analyzer, and the contents of Na and Mo were determined by the atomic-absorption method.

*Diammonium Bis{μ-[(mercapto-κ*S*:κ*S*)acetato(2−)-κ*O*]}bis[(mercapto-κ*S*)acetato(2−)-κ*O*]dioxodimolybdate(2−)(*Mo−Mo*)* (**1**): NaOH (1.87 g), $HSCH_2COOH$ (4.0 ml), $(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O$ (3.13 g), and NH_4Cl (2.5 g) were dissolved successively in H_2O. The soln. was adjusted to pH 3.8 by AcOH and then kept at r.t. without further disturbance for three weeks, yielding 2.27 g (41.35% based on Mo) of **1**. Red brown crystals. Anal. calc.: C 15.49, H 2.60, Mo 30.93, N 4.52, S 20.67; found: C 15.34, H 2.45, Mo 31.12, N 4.78, S 20.76.

*Ammonium Trisodium Hexakis{μ-[(mercapto-κ*S*:κ*S*)acetato(2−)-κ*O*]}bis[(mercapto-κ*S*)acetato(2−)-κ*O*]dioxotetramolybdate(4−)(3*Mo−Mo*) Decahydrate* (**2**). To an aq. soln. (20 ml) of **1** (0.50 g), $HSCH_2COOH$ (0.2 ml), and NaCl (1.10 g), $NH_2NH_2 \cdot 2\,HCl$ (0.11 g) was added and stirred for 5 min. Then the mixture was kept for one month to give *ca.* 10% (based on Mo of **2**. Dark brown plate crystals.

Alternatively, NaOH (2.0 g), $(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O$ (2.35 g), and $NH_2NH_2 \cdot 2\,HCl$ (0.29 g) were successively dissolved in a soln. of NaOH (2.0 g) and $HSCH_2COOH$ (5.0 ml) in H_2O (25 ml). After acidification by 10% HCl soln. (pH 4.2), the mixture was kept at r.t. for one week without further disturbance: 2.86 g (61.32% based on Mo) of **2**. Dark brown plate crystals. UV/VIS (H_2O): 225 ($1.3 \cdot 10^5$), 380 ($5.9 \cdot 10^4$). IR (KBr): 3435*s* ($\tilde{\nu}(H_2O)$), 2970*m*, 2920*m* ($\tilde{\nu}$(C−H)), 1608 v*s* ($\tilde{\nu}$(C=O)), 1323*s* ($\tilde{\nu}$(C−S)), 1217*m*, 1147*m* ($\tilde{\nu}$(C−C)), 933*s* ($\tilde{\nu}$(Mo=O)), 885*m*, 781*m*, 700*m*, 553*m* ($\tilde{\nu}(Mo{-}O_{ligand})$), 459*m*, 409*w*, 374*m*, 351*m*, 332*w*, 285*w*, 216*w*, 197*w*,

Table 1. *Crystallographic Data for* $(NH_4)_2[Mo_2O_2(\mu\text{-}SCH_2COO)_2(SCH_2COO)_2]$ (**1**) *and* $(NH_4)Na_3[Mo_4O_2(\mu\text{-}SCH_2COO)_6(SCH_2COO)_2] \cdot 10\,H_2O$ (**2**)

	1	**2**
Formula	$C_8H_{16}Mo_2N_2O_{10}S_4$	$C_{16}H_{40}Mo_4NNa_3O_{28}S_8$
M_r	620.35	1403.70
Crystal system	monoclinic	triclinic
Space group	*P*2(1)/*n*	*P*(−1)
Temperature [°]	293(2)	293(2)
Crystal size [mm]	0.12 × 0.104 × 0.09	0.15 × 0.12 × 0.10
Unit-cell parameters	$a = 11.7595(4)$ Å	$a = 12.7873(2)$ Å
	$b = 5.8320(10)$ Å	$b = 14.05640(10)$ Å
	$c = 13.9728$ Å	$c = 15.0112(2)$ Å
	$\alpha = 90°$	$\alpha = 109.470(10)°$
	$\beta = 96.587(2)°$	$\beta = 110.6020(10)°$
	$\gamma = 90°$	$\gamma = 101.6020(10)°$
	$V = 951.95(5)$ Å^3	$V = 2220.79(5)$ Å^3
	$Z = 2$	$Z = 2$
Radiation, λ[Å]	Mo*Kα*, 0.71073	Mo*Kα*, 0.71073
Absorption coefficient [mm^{-1}]	1.806	1.598
Density [g/cm^3]	2.164	2.099
θ Range for data collection	$2.15 \leq \theta \leq 24.99$	$1.61 \leq \theta \leq 25.05$
h, *k*, *l* Range	$-13 \leq h \leq 13$, $-6 \leq k \leq 6$, $-10 \leq l \leq 16$	$-15 \leq h \leq 14$, $-12 \leq k \leq 16$, $-17 \leq l \leq 17$
Data, restraints, parameters	1634, 4, 135	7640, 0, 541
Absorption correction	SADABS	SADABS
Reflections collected	2821	11350
Unique reflections (*R*(int))	1634 (0.0244)	7640 (0.0226)
Max./min. effective transmission	1.000000 and 0.742553	1.000000 and 0.809789
Goodness-of-fit on F^2	1.106	1.064
Final *R* indices ($I > 2 \approx (I)$)	0.0378, 0.0879	0.0400, 0.0948
R_1, wR_2 (all data)	0.0542, 0.1005	0.0574, 0.1068
Max. shift (Δ/σ) in final cycle	0.000	0.000
Largest diff. peak/hole [e · Å^{-3}]	0.610 and −0.604	0.742 and −0.593

Table 2. *Important Bond Lengths* [Å] *and Angles* [°] *for Compounds* **1** *and* **2**. For symmetry transformations used to generate equivalent atoms, see *Footnotes*.

$(NH_4)_2[Mo_2O_2(\mu\text{-}SCH_2COO)_2(SCH_2COO)_2]$ (**1**)

Mo(1)–O(1)	1.669(4)	S(1)–C(2)	1.814(5)	O(2)–C(1)	1.291(7)
Mo(1)–O(4)	2.071(4)	S(1)–Mo(1)[a])	2.4500(15)	O(2)–H(1A)	1.91(3)
Mo(1)–O(2)	2.152(4)	S(1)–S(2)[a])	3.216(2)	O(2)–N(1)	2.826(7)
Mo(1)–S(2)	2.3822(16)	S(1)–S(1)[b])	3.512(3)	O(3)–C(1)	1.220(7)
Mo(1)–S(1)[a])	2.4500(15)	S(2)–C(4)	1.813(7)	O(4)–C(3)	1.299(7)
Mo(1)–S(1)	2.4951(15)			O(5)–C(3)	1.220(8)
Mo(1)–Mo(1)[a])	3.0272(9)			C(1)–C(2)	1.526(9)
D–H···A				*d*(D···A)	<(DHA)
N(1)–H(1A)···O(2)		0.94(2)	1.91(3)	2.826(7)	165(9)
N(1)–H(1B)···O(3)[c])		0.95(2)	1.85(3)	2.791(7)	170(10)
N(1)–H(1C)···O(5)[d])		0.93(2)	1.90(3)	2.803(7)	163(7)
N(1)–H(1D)···O(4)[e])		0.94(2)	2.05(4)	2.884(7)	148(6)

[a]) $-x+2, -y+1, -z+1$. [b]) $-x+2, -y, -z+1$. [c]) $-x+3/2, y+1/2, -z+3/2$. [d]) $-x+1, -y+1, -z+1$. [e]) $x, y+1, z$.

$(NH_4)Na_3[Mo_4O_2(\mu\text{-}SCH_2COO)_6(SCH_2COO)_2]\cdot 10\ H_2O$ (**2**)

Mo(1)–O(17)	1.681(4)	Mo(2)–S(4)	2.4311(14)	Mo(4)–O(13)	2.174(4)
Mo(1)–O(1)	2.100(4)	Mo(2)–S(2)	2.4774(14)	Mo(4)–S(8)	2.3978(17)
Mo(1)–O(3)	2.170(4)	Mo(2)–Mo(3)	2.7580(6)	Mo(4)–S(6)	2.4329(14)
Mo(1)–S(1)	2.3856(15)	Mo(3)–O(7)	2.084(4)	Mo(4)–S(7)	2.4773(15)
Mo(1)–S(3)	2.4293(14)	Mo(3)–O(11)	2.145(4)	S(1)–C(1)	1.809(7)
Mo(1)–S(2)	2.4805(15)	Mo(3)–S(4)	2.3900(14)	S(2)–C(3)	1.808(6)
Mo(1)–Mo(2)	2.9729(6)	Mo(3)–S(6)	2.3952(14)	S(3)–C(5)	1.819(6)
Mo(2)–O(9)	2.060(4)	Mo(3)–S(5)	2.4287(14)	S(4)–C(7)	1.818(6)
Mo(2)–O(5)	2.142(4)	Mo(3)–S(7)	2.4801(14)	S(5)–C(9)	1.817(6)
Mo(2)–S(5)	2.3865(14)	Mo(3)–Mo(4)	2.9972(7)	S(6)–C(11)	1.820(6)
Mo(2)–S(3)	2.4007(14)	Mo(4)–O(18)	1.680(4)	S(7)–C(13)	1.816(6)
		Mo(4)–O(15)	2.120(4)	S(8)–C(15)	1.809(8)
d(D···A)		*d*(D···A)		*d*(D···A)	
O(51)–O(10)[a])	2.806(6)	O(52)–O(59)[h])	2.854(7)	O(59)–O(3)[a])	2.893(6)
O(51)–O(60)[h])	2.790(6)	O(53)–O(17)[j])	2.853(6)	N(1)–O(53)[k])	2.836(9)
O(52)–O(10)[i])	2.723(6)	O(55)–O(56)[i])	2.767(8)	N(1)–O(54)[k])	2.867(9)
		O(57)–O(13)[d])	2.878(7)	N(1)–O(6)[a])	2.889(7)

[a]) $x+1, y, z$. [b]) $x, y-1, z$. [c]) $x, y-1, z-1$. [d]) $-x+1, -y+3, -z+2$. [e]) $x-1, y, z$. [f]) $-x+2, -y+13, -z+2$. [g]) $-x+3, -y+3, -z+2$. [h]) $-x+2, -y+2, -z+2$. [i]) $x, y+1, z$. [j]) $x-1, y, z-1$. [k]) $x, y+1, z+1$.

189*w*, 147*m*. *Raman* ($\lambda = 1064$ nm): 2973*m*, 1919*s*, 1398*w*, 1374*w*, 1336*w*, 1220*w*, 937*s*, 782*m*, 763*w*, 705*w*, 537*w*, 462*m*, 399*w*, 283*w*, 264*w*, 346*w*, 283*m*, 252*w*, 216*s*, 167*s*, 136*vs*. Anal. calc.: C 13.69, H 2.87, Mo 27.34, N 0.99, Na 4.91, S 18.27; found: C 13.70, H 2.91, Mo 28.01, N 0.85, Na 5.13, S 17.78.

X-Ray Crystallographic Analysis. Suitable single crystals for **1** ($0.12 \times 0.104 \times 0.09$ mm) and **2** ($0.45 \times 0.12 \times 0.10$ mm) were mounted on a glass fiber for data collection on a *Siemens SMART-CCD* diffractometer with graphite-monochromated MoK_α radiation (λ 0.71073 Å) at r.t. In both cases, an empirical absorption correction by SADABS was applied to the intensity data. The structures were solved by direct methods and by successive *Fourier* difference synthesis, and refined by the full-matrix least-squares minimization of $(\Sigma w(F_o - F_c)^2$ with anisotropic thermal parameters for all non-H-atoms. The H-atoms riding on C-atoms were located theoretically, and a *Fourier* difference synthesis revealed the positions of all H-atoms of NH_4^+ in **1**. All H-atoms were refiened with isotropic thermal parameters, giving rise to final convergence with $R_1 = 0.0378$ and $wR_2 = 0.0879$ for **1** and $R_1 = 0.0400$ and $wR_2 = 0.0948$ for **2** with $I > 2\sigma(I)$. Crystal parameters and other experimental details of the data collection for **1** and **2** are summarized in *Table 1*, and selected bond lengths and angles in *Table 2*. Crystallographic data for the structures reported here have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication no. CCDC-183114 and CCDC-177732, respectively.

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