Charge-Transfer Complexes of Metal Dithiolenes, XXII[◇]

Bis(maleonitriledithiolato)oxomolybdate(IV)–Bipyridinium Ion Pairs☆

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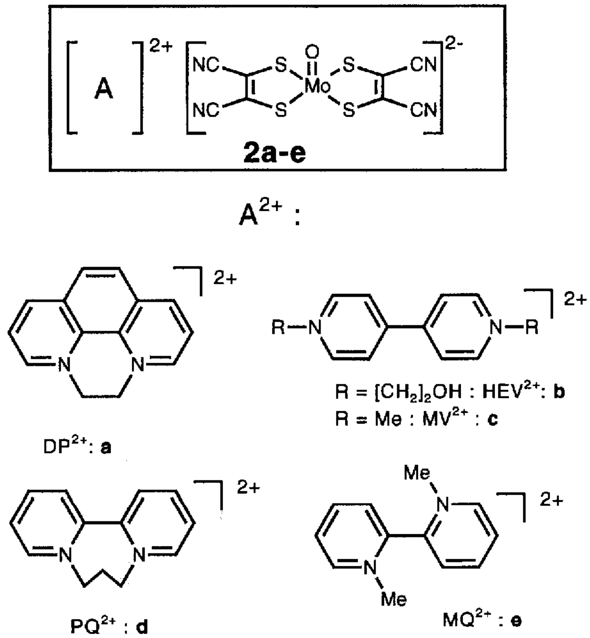
The oxomolybdenum complex $(NBu_4)_2[MoO(mnt)_2]$ (mnt^{2-} = maleonitriledithiolate) **2** was characterized by X-ray structural analysis. By metathetic reaction with bipyridinium salts AX_2 ion pair charge-transfer complexes of composition $\{A^{2+}[MoO(mnt)_2]^{2-}\}$ were isolated. Although a plot of the energy of the ion pair charge-transfer band vs. the driving force of electron transfer from the dianion to the dication afforded a straight line, the slope of 0.45 suggests significant deviations from the Hush-Marcus model. When bis(2-hydroxyethyl)viologen is the acceptor, in addition to the supramolecular charge-transfer interaction, hydrogen bridges are introduced between the two components as indicated by IR and X-ray diffraction analysis.

Within our work on the control of physical and chemical properties through modification of the supramolecular charge-transfer interaction in ion pair complexes of the type $\{A^{2+}[ML_2]^{2-}\}$, wherein A^{2+} is a bipyridinium acceptor, L an ethylene-1,2-dithiolate lake maleonitrile-1,2-dithiolate (mnt^{2-}) or 2-thioxo-1,3-dithiole-4,5-dithiolate ($dmit^{2-}$), and M = Ni, Pd, Pt, it turned out that the conductivity of the solids[2] and photoinduced electron transfer to O_2 in solution[3] can be easily tuned by changing the redox potentials of the two components. In an attempt to increase and modify the supramolecular interaction through hydrogen bonding we now introduced an OH group in the bipyridinium acceptor and an oxo ligand in the dithiolene metalate part. In the following we report on the synthesis and structure of redox-active ion pairs between the dianionic donor $[MoO(mnt)_2]^{2-}$ and five bipyridinium dicationic acceptors (A^{2+}) including the new *N,N'*-bis(2-hydroxyethyl)-4,4'-bipyridinium (HEV^{2+}) compound (Scheme 1). In addition to the tetraphenylphosphonium and tetraalkylammonium salts[4] of $[Mo^{IV}O(mnt)_2]^{2-}$ the corresponding complexes of the $dmit^{2-}$ ligand[5], of benzene-1,2-dithiolate[6] (bdt^{2-}), of toluene-3,4-dithiolate and its triphenylsilyl-substituted derivatives[7] were described recently. These are model compounds of molybdenum oxidoreductases since their kinetic inertness seems to prevent the undesired formation of μ-oxo-bridged dinuclear complexes during oxygen atom transfer reactions[4c,7]. The structure and EPR parameters of a mono(dithiolene)oxomolybdenum(V) complex were recently reported in connection with the properties of sulfite oxidase[8].

Scheme 1



Results and Discussion

The procedure as described[5] for $(NBu_4)_2[MoO(dmit)_2]$ (**1**) was employed for the synthesis of the known[4] complex $(NBu_4)_2[MoO(mnt)_2]$ (**2**). From the X-ray analysis (Figure 1) a structure analogous to that of the corresponding bdt^{2-} complex[6] is revealed. The coordination geometry around molybdenum is square-pyramidal and the angle between the Mo=O bond (167.0±0.6 pm) and each of the planes formed by Mo and the two sulfur and two sp^2-carbon

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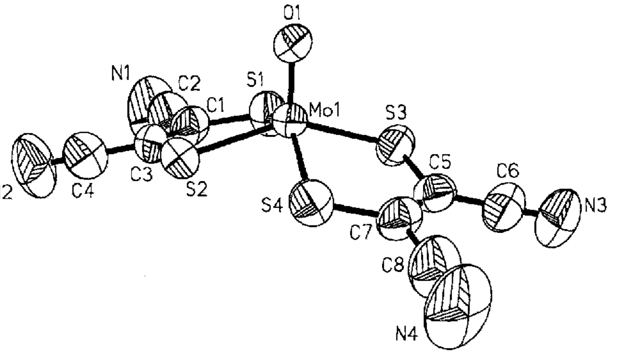
[◇] Part XXI: Ref.[1].

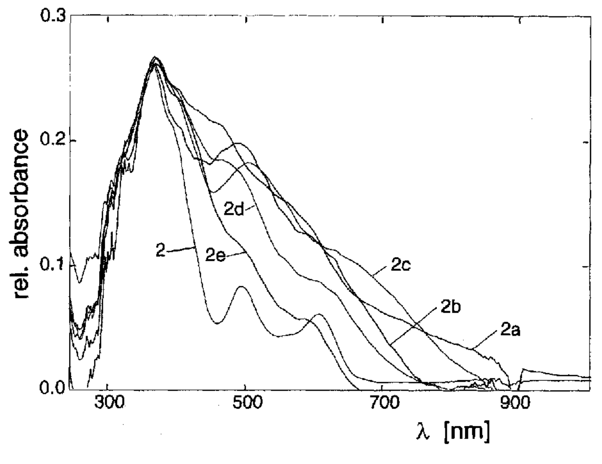
atoms of the mnt^{2-} ligand is 108 °. The molybdenum atom is located 77 pm above the plane formed by the four sulfur atoms. Mo−S and bond lengths within the mnt^{2-} ligand will be discussed later (see Table 1).

Figure 1. Molecular structure of the dianion of **2**



The electronic absorption spectrum of **2** in DMSO exhibits the well-known intraligand (IL) bands of mnt^{2-} at 259 (32240), 335 (4790) and 369 nm (10640) (in parentheses: ε [$l mol^{-1} cm^{-1}$]) and two shoulders, the positions of which do not depend on solvent polarity. This part resembles the spectrum of the d^{10} complex $(NBu_4)_2[Zn(mnt)_2]$[9]. Two weak bands at 500 (120) and 613 nm (60) are assigned to metal-centered (MC) transitions localized at the d^2 molybdenum(IV) atom, as they occur also in comparable d^1 and d^2 systems $[VO(OH_2)_4]^{2+}$[10] and $[MNX_4]^-$. M = Ru(VI), Os(VI), X = Cl, Br[11]. In the diffuse reflectance spectrum of the powder (Figure 2) the 255 nm band is missing due to absorption by the Al_2O_3 standard while the other IL bands are slightly blue-shifted as compared with solution. The same effect is observed for the MC bands which appear at 496 and 608 nm.

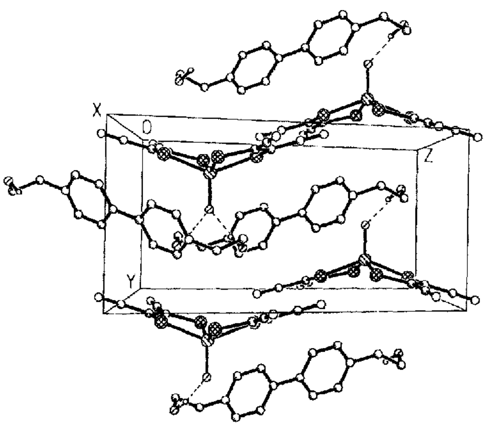
Figure 2. Diffuse reflectance spectra



The ion pair charge-transfer (IPCT) complexes $\{A^{2+}[MoO(mnt)_2]^{2-}\}$ are obtained as amorphous powders by combining acetone solutions of **2** and the acceptor salts. In some cases the use of the hexafluorophosphate salts instead of simple halides is necessary in order to obtain analytically pure materials. As bipyridinium acceptors (Scheme 1) were employed $DP(PF_6)_2$ (−0.03 V, vs. SCE, MeCN), $(HEV)Br_2$ (−0.40 V), $(MV)Cl_2 \cdot 3\,H_2O$ (−0.45 V), $PQ(PF_6)_2$ (−0.56) V), and $MQ(BF_4)_2$ (−0.76 V). Complex **2** in acetonitrile solution exhibits a reversible oxidation at 0.40 V (vs. SCE)[4c]. From these redox potentials the driving force of electron transfer (ΔG_{12}) from $[MoO(mnt)_2]^{2-}$ to the different acceptors A^{2+} is calculated to span a range of 0.6 V.

The structures of **2b** and **2c** were solved by X-ray diffraction (Figures 3, 4). In both compounds the $[MoO(mnt)_2]^{2-}$ ions have the same overall structure as in **2** except that the Mo−O bond is elongated by about 2 and 1 pm to 171.3±0.4 and 169.7±0.3 pm in **2b** and **2c**, respectively (Table 1). The HEV^{2+} acceptor of **2b** is planar while the two pyridinium rings of the two independent ion pairs of **2c** are twisted by 11 and 28 °. In both compounds the packing of the dianions creates helical pseudo-columns and the dications are located between them. The average Mo−Mo distance is 790 and 668 pm in **2b** and **2c**, respectively. As observed in other dithiolene metalate−viologen ion pairs[12], shortest interionic distances of 309 (**2b**) and 336 (**2c**) occur between the nitrogen atom of the donor and the carbon atom *ortho* to the positively charged nitrogen of the acceptor. The shorter distance in the case of **2b** may be induced by the presence of the interionic hydrogen bond between the oxomolybdenum and hydroxyl groups as indicated by the corresponding O−H distance of 188 pm. This induces a helical donor-acceptor arrangement as depicted schematically in Figure 5.

Figure 3. Molecular structure of **2b** in the crystal. Half of the unit cell content is given



It is known that in tetraalkylammonium dithiolene metalates the ν(CS) and ν(C=C) vibrations are shifted to higher and lower wave numbers, respectively, when the dianion is oxidized to the monoanion[13]. Therefore, one would expect a parallel behavior upon increasing the reduction potential of the acceptor, i. e. exchanging NBu_4^+ for the series of bipyridinium dications depicted in Scheme 1. Contrary to that, there is no obvious trend in the positions of the ν(C=C) bands whereas all ν(CS) stretching vibrations appear at lower wave numbers as compared to **2** (881 cm^{-1}, Table 2). In the acceptor sequence PQ^{2+}, MV^{2+}, DP^{2+} the shift increase from 25 (**2d**) over 31 (**2c**) to 49 cm^{-1} (**2a**) may suggest that the increasing acceptor power is responsible for

Figure 4. Molecular structure of **2c**

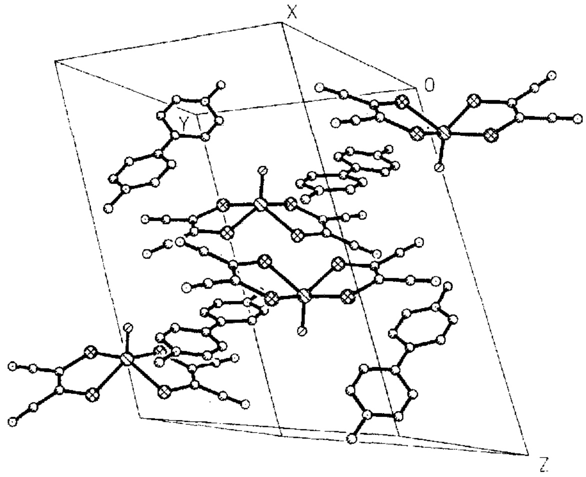


Figure 5. Schematic view of the arrangement of donor and acceptor in **2b**

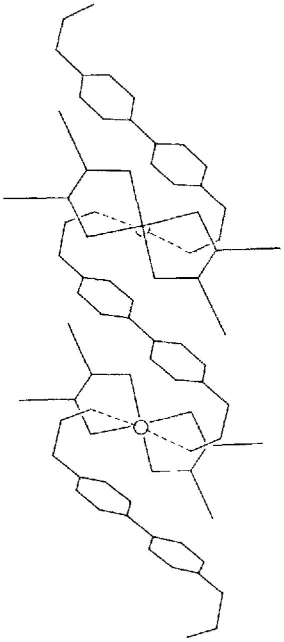


Table 1. Selected bond lengths [pm] and bond angles [°] of **2**, **2b**, and **2c**; maximum standard deviations are 1 pm and 0.7°

	2	**2b**	**2c**
Mo=O	167	171	170
Mo–S	238	238	238
S1–C1	177	176	175
S2–C3	172	174	175
S3–C5	176	176	175
S4–C7	175	174	175
C1–C3	135	137	135
S1–Mo–S2	84	84	84
S1–Mo–S3	85	85	84
S3–Mo–S4	84	84	84
S2–Mo–S4	85	85	85

the effect. However, the medium shift of 27 cm^{-1} observed for the MQ^{2+} case (**2e**) and the unique value of 66 cm^{-1} found for the HEV^{2+} complex **2b** indicate that small geometrical changes like those recently reported for iron thiolate complexes[14] may overrule the weak electronic effects. Similarly, the shift of the ν(Mo=O) band to lower wave number upon replacement of tetrabutylammonium by one of the redox-active cations is opposite as expected. It is known that lowering of the electron density in other oxomolybdenum complexes shifts this vibration to higher energy[15]. Again, the vibration of the HEV^{2+} complex appears at the exceedingly low wave number of $\tilde{\nu} = 886\ cm^{-1}$ as compared to $\tilde{\nu} = 922-928\ cm^{-1}$ observed for the other compounds. The spectra of all complexes contain the ν(CN) band at $\tilde{\nu} = 2191-2196\ cm^{-1}$

Table 2. Selected IR bands (KBr) [cm^{-1}] of **2** and **2a–e**

		$\nu_{Mo=O}$	ν_{C-S}	$\nu_{C=C}$
2	NBu_4^+	940	881	1489
2a	DP^{2+}	928	832	1487
2b	HEV^{2+}	886	815	1499
2c	MV^{2+}	922	850	1490
2d	PQ^{2+}	923	856	1493
2e	MQ^{2+}	924	854	1499

In contrast to the IR data, the UV-Vis diffuse reflectance spectra support the presence of CT interaction between the two components. As compared to **2** a general broadening of the bands as observed at wavelengths larger than 370 nm and new IPCT absorptions appear as shoulders. Since their maxima are difficult to obtain with accuracy, the concentration-independent method[16] described recently[2] was employed to obtain the corresponding onset energies E_{IPCT} of 153 (787 nm, **2a**), 172 (699 nm, **2b**), 172 (699 nm, **2c**), 176 (683 nm, **2d**), and 185 kJ/mol (648 nm, **2e**). A plot of E_{IPCT} vs. ΔG_{12}, calculated from the reduction potentials of the two components, affords a straight line (correlation coeff. = 0.9) as expected from the Hush-Marcus model[17]. However, as already observed for IPCT complexes with $[Co(mnt)_2]^{2-}$ as the donor[18], the slope of 0.45 strongly deviates from the theoretical value of 1.0.

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Experimental

All preparations were performed in dry solvents under N_2 unless noted otherwise. $Na_2MoO_4 \cdot 3\ H_2O$ (Merck), $K(PF_6$ (Aldrich), $(MV)Cl_2 \cdot 3\ H_2O$, 4,4'-bipyridyl, 2,2'-bipyridyl, 2-bromoethanol, 1,3-dibromopropane, and tetrabutylammoniumbromide were used as received (Fluka); $(pyH)_2[MoOCl_5]$[19], Na_2mnt[20], $(PQ)Br_2$[21], $(DP)Br_2$[22], and $MQ(BF_4)_2$[23] were synthesized according to literature procedures. UV-NIR and IR (in KBr) spectra were obtained as described in ref.[2]. The onset of absorbance, E_{IPCT}, was obtained by an extrapolation technique as described recently[2].

Complex **2**: By analogy with the synthesis of **1**[5], 1.40 g (8.04 mmol) of Na_2mnt and a cooled suspension of 1.81 g (4.02 mmol) of (pyH)$_2$[MoOCl$_5$] in 50 ml of EtOH were added to a solution of 1.20 g (52.0 mmol) of sodium in 50 ml of EtOH (dissolution with ice cooling). After stirring for 1 h 200 ml of MeOH were added, the ice-bath was replaced by warm water and stirring was continued overnight. Non-dissolved material was filtered off and a solution of 3.890 g (12.0 mmol) of (NBu$_4$)Br in 10 ml of MeOH was added. After standing over night in the refrigerator, the formed precipitate was separated, washed twice each with precooled portions of 10 ml of EtOH and MeOH and dried at room temp. in vacuo. From the filtrate additional product was obtained by the same procedure. Yield: 1.46 g (45%) of gray-brown needles of **2**. – $C_{40}H_{72}MoN_6OS_4$ (877.25): calcd. C 54.77, H 8.27, N 9.58, S 14.62; found C 54.78, H 8.35, N 9.63, S 14.67. – Crystals for X-ray analysis were obtained when EtOH was carefully added to a saturated MeOH solution and the resulting mixture was left at room temp. for a few days.

N,N'-Ethylene-1,10-phenanthrolinium Bis(hexafluorophosphate): To a solution of 3.68 g (10.0 mmol) of (DP)Br$_2$ in 100 ml of H_2O was added dropwise in air a solution of 3.68 g (20 mmol) of K(PF$_6$) in 120 ml of H_2O. After 1 h the precipitate was filtered off, washed several times with H_2O and dried in a desiccator. Yield: 2.89 g (58%), slighly brown powder. – $C_{14}H_{12}F_{12}N_2P_2$ (498.19): calcd. C 33.75, H 2.43, N 5.62; found C 33.81, H 2.31, N 5.44.

N,N'-Bis(2-hydroxyethyl)-4,4'-bipyridinium Dibromide: As described in ref.[24] 7.81 g (50.0 mmol) of 4,4'-bipyridyl and 8.52 ml (15.0 g, 120 mmol) of 2-bromoethanol were heated in 100 ml of DMF at 110°C for 22 h. After cooling to room temp. the gray precipitate was filtered off and recrystallized from a mixture of 60 ml of MeOH and 20 ml of H_2O. Yield: 11.39 g (61%), lightbrown powder. – $C_{14}H_{16}Br_2N_2O_2$ (326.22): calcd. C 41.41, H 4.47, N 6.90; found C 41.41, H 4.44, N 6.72.

N,N'-Propylene-2,2'-bipyridinium Bis(hexafluorophosphate): Prepared by analogy with DP(PF$_6$)$_2$ by adding a solution of 3.68 g (20 mmol) of K(PF$_6$) in 120 ml of H_2O to a solution of 2.78 g (10 mmol) of (PQ)Br$_2$ in 100 ml of H_2O. Yield: 3.75 g (77%), white powder. – $C_{13}H_{14}F_{12}N_2P_2$ (488.19): calcd. C 31.98, H 2.89, N 5.74; found C 32.12, H 2.74, N 5.46.

Complex **2a**: To a solution of 0.28 g (0.314 mmol) of **2** in 10 ml of acetone was added dropwise with stirring a solution of 0.16 g (0.314 mmol) of DP(PF$_6$)$_2$ in 10 ml of MeOH. The dark precipitate, formed immediately, was filtered off after a few hours, washed three times with 2-ml portions of acetone and dried in vacuo. Yield: 0.17 g (90%), brown powder. – $C_{22}H_{12}MoN_6OS_4$ (600.57): calcd. C 44.00, H 2.01, N 13.99, S 21.36; found C 44.29, H 2.03, N 13.79, S 21.58.

Complex **2b**: Prepared by dropwise addition of a solution of 0.47 g (0.530 mmol) of **2** in 10 ml of acetone to a warm solution of 0.17 g (0.530 mmol) of (HEV)Br$_2$ in 20 ml of MeOH and 5 ml of H_2O. Yield: 0.13 g (38%), black powder. – $C_{22}H_{18}MoN_6O_3S_4$ (638.62): calcd. C 41.38, H 2.48, N 13.16, S 20.08; found C 41.42, H 2.73, N 13.00, S 19.95. – Crystals for X-rax analysis were obtained when benzene was carefully added to a saturated DMSO solution and the resulting mixture was left at room temp. for a few weeks.

Complex **2c**: Prepared by dropwise addition of a solution of 0.13 g (0.410 mmol) of (MV)Cl$_2$ · 3 H_2O in 10 ml MeOH to a solution of 0.36 g (0.410 mmol) of **2** in 10 ml of acetone. Yield: 0.21 g (88%), black powder. – $C_{20}H_{14}MoN_6OS_4$ (578.56): calcd. C 41.52, H 2.44, N 14.53, S 22.17; found C 41.65, H 2.48, N 14.53, N 22.27. – Crystals for X-ray analysis were obtained as described for **2b** but using toluene instead of benzene.

Complex **2d**: Prepared by analogy with **2a** from 0.28 g (0.576 mmol) of PQ(PF$_6$)$_2$ and 0.51 g (0.576 mmol) of **2**. Yield: 0.28 g (96%), black powder. – $C_{21}H_{14}MoN_6OS_4$ (590.580): C 42.71, H 2.39, N 14.23, S 21.72; found C 42.86, H 2.38, N 14.24, S 21.83.

Complex **2e**: Prepared by analogy with **2a** from 0.20 g (0.564 mmol) of MQ(BF$_4$)$_2$ and 0.50 g (0.564 mmol) of **2a**. Yield: 0.16 g (49%), red-brown powder. – $C_{20}H_{14}MoN_6OS_4$ (578.559): calcd. C 41.52, H 2.44, N 14.53, S 22.17; found C 41.60, H 2.35, N 14.49, S 22.27.

X-ray Analyses: Automated four-circle diffractometer (Siemens P4), Mo-K_α radiation, graphite monochromator, T = 298 K, ω-scan speed 3.0–30°/min. Structure solution by direct methods (SHELXTL-PLUS), anisotropic refinement of non-hydrogen atoms; the positions of all hydrogen atoms were taken from a difference fourier analysis and fixed at these coordinates.

Complex **2**: $C_{40}H_{72}MoN_6OS_4$ (877.3), a = 12.640(4), b = 15.699(10), c = 25.956(8) Å, β = 102.58(3)°, Z = 4, d(calcd.) = 1.16 g/cm^3, monoclinic, $P2_1/c$. Crystal size: 0.80 × 0.70 × 0.50 mm, linear absorption coefficient $\mu = 0.461$ mm^{-1}, scan range = $3° < 2\Theta < 54°$, in $-16 \le h \le 2$, $-15 \le k \le 19$, $-31 \le l \le 33$, 15253 reflections collected, 10822 independent reflections, 4557 observed reflections [$F < 4\sigma(F)$]. Because of rather high temperature coefficients the carbon atoms of the terminal methyl groups were refined isotropically without H atoms. Number of parameters = 430, data-to-parameter ratio = 10.6:1, R = 0.067, R_w = 0.057, GOF = 2.94, largest difference peak 0.61 e/Å^3.

Complex **2b**: $C_{22}H_{18}MoN_6O_3S_4$ (638.62), a = 21.605(4), b = 7.861(3), c = 16.691(4) Å, β = 112.97(2)°, Z = 4, d(calcd.) = 1.63 g/cm^3, monoclinic, $C2/c$. Crystal size: 0.70 × 0.50 × 0.50 mm, μ = 0.860 mm^{-1}, scan range $3° < 2\Theta < 54°$, in $-27 \le h \le 12$, $0 \le k \le 10$, $-19 \le l \le 21$, 4161 reflections collected, 2864 independent reflections, 2311 observed reflections [$F > 4\sigma(F)$], Number of parameters = 164, data-to-parameter ratio = 14.1:1, R = 0.039, R_w = 0.036, GOF = 2.38, largest difference peak 0.98 e/Å^3.

Complex **2c**: $C_{20}H_{14}MoN_6OS_4$ (578.56), a = 10.606(3), b = 14.570(5), c = 17.126(4) Å, α = 110.87(2), β = 94.73(2), γ = 98.25(2)°, Z = 4, d(calcd.) = 1.59 g/cm^3, triclinic, $P1$. Crystal size: 0.60 × 0.40 × 0.20 mm, μ = 0.911 mm^{-1}, scan range $3° < 2\Theta < 54°$, in $-13 \le h \le 4$, $-18 \le k \le 18$, $-21 \le l \le 21$, 13115 reflections colllected, 10652 independent reflections, 6312 observed [$F > 4\sigma(F)$]. Number of parameters = 577, data-to-parameter ratio = 10.9:1, R = 0.036, R_w = 0.033, GOF = 1.55, largest difference peak 1.01 e/Å^3.

Further details of the crystal structure investigations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-401837, -401836, and -401835 for **2**, **2b**, and **2c**, respectively.

[☆] Dedicated to Professor *Herrmann Rau* on the occasion of his 60th birthday.

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