of the interactions of fluorine atoms in the anions with the apex and base of the $As_3S_4^+$ cations, the packing of these compounds consists of rows of alternating anions and cations along *a* (Figure 2).

In $As_3Se_4^+SbF_6^-$ the positions of the fluorine atoms in the hexafluoroantimonate anion are not as well defined as those in the anions with the $As_3S_4^+$ cation so that some of the contact distances in the former structure are not as reliable. However, from the change in the symmetry of the structure and the geometry of the contacts listed in Table IV it may be noted that there are some subtle differences in the contacts to the $As_3Se_4^+$ cation from those in the $As_3S_4^+$ cation (Figure 8). In particular, the three atoms in the base of the cation are involved in three unsymmetrical fluorine bridges to the fluorine atoms in two anions. These contacts are weaker than those to the $As_3S_4^+$ cations and are close to the van der Waals limits [As(2)···F(3) = 3.14 Å, Se(2)···F(3) = 3.39 Å, and As(2)···F(4) = 3.26 Å (×2)]. It is also worthy of note that the angles Se(1)–As(2)···F(3) and Se(3)–Se(2)···F(3) are 162° and 158°, respectively. The shortest interionic contact in the $As_3Se_4(SbF_6)$ structure of length 3.02 Å is to the bridging selenium atom Se(3) and is collinear with the Se(2)–Se(3) primary bond [Se(2)–Se(3)···F(2) is 179.0 (6)°]. A similar contact to the other bridging selenium atom Se(1) is, however, poorly defined [Se(1)···F(2) = 3.21 (11) Å, As(1)–Se(1)···F(2) = 156°]. Another feature of the contacts to the $As_3Se_4^+$ cation is the absence of any short contacts to the apical arsenic atom As(1). The short anion–cation contacts observed in the present structures are analogous to those observed in the sulfur–nitrogen cations $S_3N_2^{+}\cdot$, $S_6N_4^{2+}$, and $S_4N_3^+$ (all of which principally involve the S–S bond in each ring[57]), the mixed S–Se–N cation $Se_4S_2N_4^{2+}$ (involving the diselenide bond),[58] and the homo- and heteropolyatomic cations of the group 6 elements. These charge-transfer contacts usually reflect the charge distribution in the cation and presumably play a small but nonetheless significant role in the stabilization of the cations involved.

The average antimony–fluorine bond length in the anion of $(As_3Se_4)(SbF_6)$ is 1.85 (4) Å which is similar to the bond length in $K(SbF_6)$;[55] cis and trans angles in this anion deviate by up to 5° from 90° to 180°. A view of the packing of $(As_4Se_4)(SbF_6)$ is given in Figure 3.

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Registry No. $As_3S_4(AsF_6)$, 77846-58-3; $As_3S_4(SbF_6)$, 77825-63-9; $As_3Se_4(AsF_6)$, 77825-65-1; $As_3Se_4(SbF_6)$, 77825-66-2; α-As_4S_3, 12512-13-9; α-As_4S_4, 12279-90-2; AsF_5, 7784-36-3; SbF_5, 7783-70-2; $S_8(AsF_6)_2$, 33248-05-4.

Supplementary Material Available: Listings of structure factor amplitudes (26 pages). Ordering information is given on any current masthead page.

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Contribution from the Chemistry Departments, University College, Cork, Republic of Ireland,
and University of Guelph, Guelph, Ontario N1G 2W1, Canada

Transition-Metal Complexes of Poly(1-pyrazolyl)borate Ligands. 2.[1] Crystal and Molecular Structure of (Hydrotris(3,5-dimethyl-1-pyrazolyl)borato)dicarbonyl(*p*-chlorobenzenethiolato)molybdenum(II) Acetone Solvate

TADGH BEGLEY,[2a] DAVID CONDON,[2a] GEORGE FERGUSON,*[2b] FERGUS J. LALOR,[2a]
and MASOOD A. KHAN[2b]

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Crystals of the acetone solvate of $HB(Me_2pz)_3Mo(CO)_2SC_6H_4Cl$, a formally 16-electron Mo(II) complex, are triclinic, space group $P\bar{1}$, with two formula units in a unit cell of dimensions a = 10.355 (1) Å, b = 12.100 (1) Å, c = 13.433 (1) Å, α = 103.43 (1)°, β = 94.31 (1)°, and γ = 113.74 (1)°. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations to a final R value of 0.038 for 3247 reflections with $I > 3.0\sigma(I)$. The molybdenum atom has slightly distorted octahedral coordination with the pyrazolylborate ligand occupying three *facial* sites. The Mo–S distance 2.305 (1) Å is indicative of considerable double-bond character; other dimensions include Mo–C = 1.969 and 1.977 (3) Å, Mo–N(trans to S) = 2.169 Å, and Mo–N(trans to CO) = 2.220 and 2.221 (1) Å. The acetone of solvation is present with partial occupancy and lies in cavities between the molecules of the complex.

Introduction

An interesting aspect of the chemistry of poly(1-pyrazolyl)borate ligands[3] is that the introduction of appropriate substituents onto the carbon atoms of the pyrazole rings can effect major changes in the electronic characteristics and steric demand of the ligands while leaving the symmetry unchanged.[4] In the earliest investigation of this phenomenon Trofimenko demonstrated that the carbonyl anion $HB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_3^-$ reacted in an anomalous fashion with allyl halides,[5] arenediazonium cations,[4] and arenesulfonyl

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0020-1669/81/1320-3420$01.25/0

halides.[5] We have reinvestigated the latter two reactions and find that the anomalous behavior of the anion toward diazonium salts reflects the electronic effect of the substituents on the ligand rather than steric phenomena.[6] We report here the structure of the main product of the anomalous reaction with sulfonyl halides.

The anion $HB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_3^-$ reacted with *p*-chlorobenzenesulfonyl chloride to yield the monomeric arenethiolato complex $HB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_2SC_6H_4Cl$-*p* (**1**) (already described by Trofimenko[4]) together with a complex mixture of other products, which had not been reported previously and which are currently under investigation. The complex **1** is formally a 16-electron Mo(II) species if we assume that the arenethiolato ligand behaves as a two-electron anionic ligand, ArS^-. For this reason and since complexes with terminal rather than bridging thiolato ligands are not very common[4], the structure of the compound has been established by X-ray crystallographic methods.

Experimental Section

Trofimenko's procedure[4] was used to prepare complex **1** from *p*-chlorobenzenesulfonyl chloride and $(C_2H_5)_4NHB(3,5\text{-}(CH_3)_2pz)_3Mo(CO)_3$ on a 0.01 molar scale. Purification of the crude product by dry-column chromatography on alumina, eluting with 1:1 ether–hexane, gave a low yield (ca. 10%) of the red analytically pure *p*-chlorobenzenethiolato complex together with several other products, which are currently being investigated.

X-ray Data Collection. Approximate unit cell parameters and space group information were obtained from a preliminary set of precession (Mo Kα radiation, λ = 0.71069 Å) and Weissenberg (Cu Kα radiation, λ = 1.5418 Å) photographs. Accurate cell parameters were obtained via a least-squares procedure applied to diffractometer setting angles of 12 reflections ($10 < \theta < 20°$ Mo Kα radiation) which were well separated in the reciprocal space.

Crystal data: $HB[(CH_3)_2C_3HN_2]_3Mo(CO)_2SC_6H_4Cl\cdot0.2(CH_3)_2CO$, $C_{23}H_{26}BClMoN_6O_2S\cdot0.2C_3H_6O$, M_r = 604.4, triclinic, a = 10.355 (1) Å, b = 12.100 (1) Å, c = 13.433 (1) Å, α = 103.43 (1)°, β = 94.31 (1)°, γ = 113.74 (1)°, V = 1471.4 Å^3, Z = 2, D_c = 1.36 g cm^{-1}, $F(000)$ = 617, μ(Mo Kα) = 5.7 cm^{-1}. There were no systematic absences and the space group was assumed to be $P\bar{1}$; this was confirmed by the subsequent analysis.

Diffraction data were collected in our usual way[7] using dark red crystals grown by slow evaporation of a solution in aqueous acetone. A needle crystal with maximum dimensions 0.24 × 0.36 × 0.48 mm was chosen and mounted on a eucentric goniometer head with the a axis approximately parallel to the ϕ axis. The θ–2θ scan technique and monochromated Mo Kα radiation were used with a Hilger and Watts Y290 four-circle diffractometer to record intensities of a unique hemisphere of data within the limits $2 < \theta < 23°$. The intensities of three standard reflections, monitored at 100-reflection intervals, decreased by 5.0% during the course of the data collection, and this was corrected for by appropriate scaling. The data were corrected for Lorentz and polarization factors as described previously[7] and for absorption;[8] the maximum and minimum values of the transmission coefficients are 0.89 and 0.81, respectively. In all, 4097 unique reflections were measured, of which only the 3247 with $I > 3.0\sigma(I)$ were labeled observed and used in all subsequent calculations.

Solution and Refinement of the Structure. The coordinates of the molybdenum atom were obtained from a sharpened three-dimensional Patterson synthesis, and those of the nonhydrogen atoms in the complex were found via the heavy-atom method. Two cycles of full-matrix least-squares refinement minimizing $\sum w(F_o - F_c)^2$, with anisotropic thermal parameters for nonhydrogen atoms and unit weights, lowered R to 0.06, and a difference synthesis showed electron density maxima in locations consistent with expected hydrogen atoms. These were allowed for in subsequent cycles (in geometrically expected positions with C–H and B–H 0.95 Å) and an overall U_{iso} value was refined for each type of hydrogen atom (B–H, C–H, CH_3). Four other diffuse peaks appeared clustered around a center of symmetry in the difference synthesis but too far from the main molecule to be bonded to it. After three additional cycles of full-matrix least-squares calculations with weights derived from the counting statistics, refinement had completely converged with R = 0.045 and $R' = [\sum w\Delta^2/\sum wF_o^2]^{1/2}$ = 0.047, and a difference synthesis showed the same four diffuse peaks, 1–2 e Å^{-3} in height, close to a center of symmetry. From their geometry, and integrated electron density, it was deduced that they corresponded to an acetone of solvation present with an occupancy of about 0.2 and disordered about the inversion center. When these atoms were included in additional refinement calculations, R fell to 0.035, and while there was no change in the coordinates of the complex, the acetone parameters refined to give nonsensical bond lengths and angles. Finally, when the acetone atoms were allowed for (in positions obtained from the difference synthesis[9] and with U_{iso} = 0.15 Å^2 and occupancy factor 0.2) but not refined, an additional final cycle of full-matrix least-squares calculations gave the same coordinates for the complex as in the previous cycle and final R and R' values of 0.038 and 0.041, respectively. In the calculations, the scattering factors for the nonhydrogen atoms were from ref 9 and those for hydrogen from ref 10; allowance was also made for anomalous dispersion.[12]

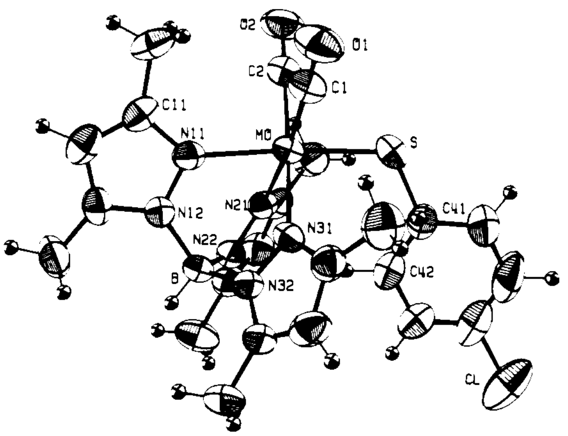

Figure 1. View of the $HB(Me_2pz_3)_3Mo(CO)_2SC_6H_4Cl$ molecule with the crystallographic numbering scheme. The probability ellipsoids are at the 50% level for nonhydrogen atoms; the hydrogen atoms are shown as spheres of arbitrary size.

Final coordinates for the atoms along with their standard deviations are in Table I; Table II gives details of molecular geometry. A view of the molecule with the outline of the crystallographic numbering scheme is in Figure 1 and the molecular packing is shown in a stereoscopic view in Figure 2. Listings of observed and calculated structure factors, thermal parameters, and hydrogen positional parameters are available as supplementary material.

Discussion

The crystal structure of $HB(Me_2pz)_3Mo(CO)_2SC_6H_4Cl\cdot0.2Me_2CO$, Figure 2, contains discrete molecules of the complex that are separated by normal van der Waals distances and are packed in layers in the yz plane with acetone molecules of solvation in partial occupancy lying around inversion centers at ($^1/_2$, 0, $^1/_2$); had there been full-site occupancy of the solvent molecules, the resulting acetone···acetone contacts across the inversion center would have been impossibly short.

The molybdenum corrdination is distorted octahedral as a consequence of the steric requirements of the pyrazolylborato ligand leading to pyrazolyl N–Mo–N angles 81.2, 82.1, and 86.9 (1)° being less than 90° as has been found in all previous (tripyrazolylborato)molybdenum complexes, e.g., 82.4° in

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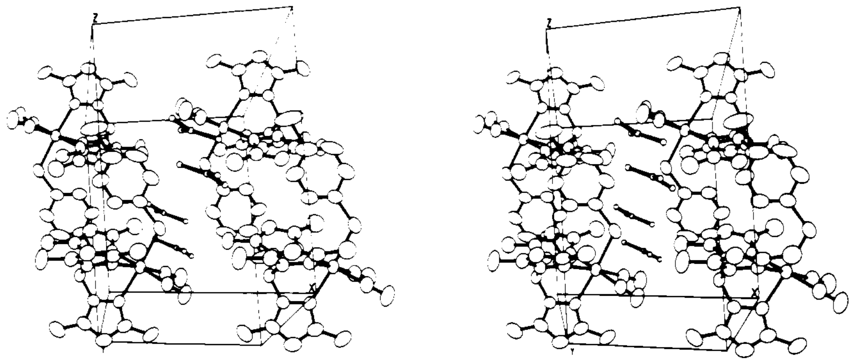

Figure 2. Stereoview of the unit cell of the acetone solvate of HB(Me$_2$pz$_3$)$_3$Mo(CO)$_2$SC$_6$H$_4$Cl.

Table I. Fractional Coordinates for HB(Me$_2$pz)$_3$Mo(CO)$_2$SC$_6$H$_4$Cl with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*
Mo	0.21304 (5)	0.35600 (4)	0.17791 (3)
Cl	−0.0131 (4)	0.1344 (2)	0.6544 (2)
S	0.3344 (1)	0.3553 (2)	0.3287 (1)
O(1)	0.4743 (5)	0.6107 (4)	0.1969 (4)
O(2)	0.4369 (4)	0.2993 (4)	0.0585 (4)
N(11)	0.0840 (5)	0.3532 (4)	0.0417 (3)
N(12)	−0.0636 (4)	0.3040 (4)	0.0338 (3)
N(21)	0.0384 (5)	0.1625 (4)	0.1445 (3)
N(22)	−0.1005 (4)	0.1439 (4)	0.1321 (3)
N(31)	0.0681 (4)	0.4236 (4)	0.2590 (3)
N(32)	−0.0787 (4)	0.3592 (4)	0.2240 (3)
C(1)	0.3747 (6)	0.5214 (6)	0.1930 (4)
C(2)	0.3488 (6)	0.3127 (5)	0.1010 (4)
C(11)	0.1100 (6)	0.3846 (5)	−0.0479 (4)
C(12)	−0.0157 (7)	0.3572 (5)	−0.1094 (4)
C(13)	−0.1240 (6)	0.3049 (5)	−0.0575 (4)
C(14)	0.2586 (8)	0.4374 (6)	−0.0707 (5)
C(15)	−0.2802 (7)	0.2542 (7)	−0.0948 (5)
C(21)	0.0357 (6)	0.0502 (5)	0.1432 (4)
C(22)	−0.1036 (7)	−0.0359 (5)	0.1324 (4)
C(23)	−0.1877 (7)	0.0241 (6)	0.1266 (4)
C(24)	0.1676 (8)	0.0304 (6)	0.1541 (5)
C(25)	−0.3482 (7)	−0.0225 (6)	0.1153 (6)
C(31)	0.0872 (6)	0.5135 (5)	0.3468 (4)
C(32)	−0.0446 (7)	0.5049 (6)	0.3678 (5)
C(33)	−0.1466 (6)	0.4070 (5)	0.2894 (4)
C(34)	0.2323 (7)	0.6065 (6)	0.4074 (5)
C(35)	−0.3044 (7)	0.3578 (7)	0.2752 (5)
C(41)	0.2279 (7)	0.2941 (5)	0.4181 (4)
C(42)	0.0800 (6)	0.2307 (5)	0.3964 (4)
C(43)	0.0064 (8)	0.1822 (5)	0.4688 (4)
C(44)	0.0808 (10)	0.1968 (7)	0.5628 (5)
C(45)	0.2267 (12)	0.2615 (9)	0.5878 (5)
C(46)	0.2995 (8)	0.3096 (7)	0.5151 (5)
B	−0.1365 (7)	0.2539 (6)	0.1206 (4)
C(3)	0.533	0.013	0.425
C(4)	0.410	0.050	0.475
C(5)	0.561	−0.093	0.383
O(3)	0.637	0.095	0.409

Table II. Principal Interatomic Distances (Å) and Angles (Deg) with Estimated Standard Deviations in Parentheses

(a) Bond Distances

Mo–S	2.305 (1)	N(32)–C(33)	1.336 (6)
Mo–N(11)	2.169 (3)	N(32)–B	1.533 (6)
Mo–N(21)	2.221 (3)	C(11)–C(12)	1.360 (6)
Mo–N(31)	2.220 (3)	C(11)–C(14)	1.497 (6)
Mo–C(1)	1.977 (3)	C(12)–C(13)	1.377 (4)
Mo–C(2)	1.969 (3)	C(13)–C(15)	1.476 (5)
Cl–C(44)	1.746 (4)	C(21)–C(22)	1.370 (4)
S–C(41)	1.778 (3)	C(21)–C(24)	1.481 (5)
O(1)–C(1)	1.142 (4)	C(22)–C(23)	1.348 (4)
O(2)–C(2)	1.158 (4)	C(23)–C(25)	1.508 (6)
N(11)–N(12)	1.384 (5)	C(31)–C(32)	1.382 (6)
N(11)–C(11)	1.357 (6)	C(31)–C(34)	1.489 (5)
N(12)–C(13)	1.338 (6)	C(32)–C(33)	1.369 (6)
N(12)–B	1.546 (6)	C(33)–C(35)	1.476 (6)
N(21)–N(22)	1.354 (5)	C(41)–C(42)	1.379 (5)
N(21)–C(21)	1.343 (6)	C(41)–C(46)	1.383 (5)
N(22)–C(23)	1.344 (6)	C(42)–C(43)	1.373 (5)
N(22)–B	1.556 (5)	C(43)–C(44)	1.365 (5)
N(31)–N(32)	1.381 (5)	C(44)–C(45)	1.363 (7)
N(31)–C(31)	1.345 (6)	C(45)–C(46)	1.372 (6)

(b) Bond Angles

S–Mo–N(11)	175.5 (1)	Mo–C(2)–O(2)	173.6 (3)
S–Mo–N(21)	96.3 (1)	N(11)–C(11)–C(12)	110.0 (3)
S–Mo–N(31)	94.1 (1)	N(11)–C(11)–C(14)	121.8 (3)
S–Mo–C(1)	86.5 (1)	C(12)–C(11)–C(14)	128.1 (3)
S–Mo–C(2)	89.0 (1)	C(11)–C(12)–C(13)	106.8 (3)
N(11)–Mo–N(21)	81.2 (1)	N(12)–C(13)–C(12)	107.9 (3)
N(11)–Mo–N(31)	82.1 (1)	N(12)–C(13)–C(15)	124.7 (3)
N(11)–Mo–C(1)	96.3 (1)	C(12)–C(13)–C(15)	127.3 (3)
N(11)–Mo–C(2)	95.0 (1)	N(21)–C(21)–C(22)	109.2 (3)
N(21)–Mo–N(31)	86.9 (1)	N(21)–C(21)–C(24)	122.7 (3)
N(21)–Mo–C(1)	173.6 (1)	C(22)–C(21)–C(24)	128.0 (3)
N(21)–Mo–C(2)	98.1 (1)	C(21)–C(22)–C(23)	107.5 (3)
N(31)–Mo–C(1)	98.6 (1)	N(22)–C(23)–C(22)	107.0 (3)
N(31)–Mo–C(2)	173.8 (1)	N(22)–C(23)–C(25)	122.0 (3)
C(1)–Mo–C(2)	76.2 (1)	C(22)–C(23)–C(25)	131.0 (3)
Mo–S–C(41)	116.5 (1)	N(31)–C(31)–C(32)	109.8 (3)
Mo–N(11)–N(12)	118.7 (3)	N(31)–C(31)–C(34)	122.5 (3)
Mo–N(11)–C(11)	135.6 (3)	C(32)–C(31)–C(34)	127.7 (3)
N(12)–N(11)–C(11)	105.6 (3)	C(31)–C(32)–C(33)	106.6 (3)
N(11)–N(12)–C(13)	109.6 (3)	N(32)–C(33)–C(32)	107.8 (3)
N(11)–N(12)–B	121.3 (3)	N(32)–C(33)–C(35)	123.7 (3)
C(13)–N(12)–B	129.1 (3)	C(32)–C(33)–C(35)	128.5 (3)
Mo–N(21)–N(22)	119.9 (3)	S–C(41)–C(42)	124.5 (2)
Mo–N(21)–C(21)	133.9 (3)	S–C(41)–C(46)	117.2 (3)
N(22)–N(21)–C(21)	105.8 (3)	C(42)–C(41)–C(46)	118.3 (3)
N(21)–N(22)–C(23)	110.5 (3)	C(41)–C(42)–C(43)	120.7 (3)
N(21)–N(22)–B	119.0 (3)	C(42)–C(43)–C(44)	119.4 (4)
C(23)–N(22)–B	130.4 (3)	C(43)–C(44)–C(45)	121.4 (4)
Mo–N(31)–N(32)	119.7 (3)	C(43)–C(44)–Cl	119.3 (4)
Mo–N(31)–C(31)	134.4 (3)	C(45)–C(44)–Cl	119.3 (3)
N(32)–N(31)–C(31)	105.6 (3)	C(44)–C(45)–C(46)	118.8 (4)
N(31)–N(32)–C(33)	110.2 (3)	C(41)–C(46)–C(45)	121.4 (4)
N(31)–N(32)–B	118.7 (3)	N(12)–B–N(22)	108.2 (3)
C(33)–N(32)–B	131.1 (3)	N(12)–B–N(32)	109.9 (3)
Mo–C(1)–O(1)	173.6 (3)	N(22)–B–N(32)	109.4 (3)

HB(pz)$_3$Mo(CO)$_2$NO[13] and 82° in HB(pz)$_3$Mo(CO)$_2$N$_2$C$_6$H$_5$.[14] Two of the Mo–N distances (Mo–N(21) = 2.221 (3) Å and Mo–N (31) = 2.220 (3) Å) are not significantly different, whereas the third (Mo–N(11) = 2.169 (3) Å) is significantly shorter; this bond length difference can be attributed to the trans effect of the carbonyl groups trans to N(21) and N(31). An exactly similar situation holds in PhB(pz)$_3$Mo(CO)$_2$C$_7$H$_7$[15] where two of the Mo–N distances (2.256 and 2.260 (3) Å trans to CO) are longer than the third (2.204 (4) Å trans to C$_7$H$_7$). The dimensions of the HB(Me$_2$Pz)$_3$ ligand are normal with mean bond lengths C–C(ring) = 1.368 (4) Å, C–CH$_3$ = 1.488 (6) Å, C–N = 1.344

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(6) Å, N–N = 1.373 (5) Å, and N–B = 1.545 (6) Å in accord with values reported previously.[1]

That the arenethiolato ligand is terminal rather than bridging is a consequence of steric crowding around molybdenum, there being no available space for another ligand. The Mo–S bond length (2.305 (1) Å) is much shorter than Mo–S single bond distances (~2.45 Å) reported for a number of molybdenum–sulfur complexes.[16] For *terminal* Mo=S bonds an average length of 2.10 (2) Å is well established.[16] From these data we would infer that the formal 16-electron character of the Mo atom in complex **1** is removed by appreciable S→Mo pπdπ bonding. Of some interest in relation to our results are the structural data reported[17] for the complexes (η^5-C_5H_5)Mo(CO)($CF_3C_2CF_3$)(SC_6H_5) (**2**) and η^5-C_5H_5)MoO($CF_3C_2CF_3$)(SC_6F_5) (**3**). Both complexes are formal 16-electron species if the ligands donate their "normal" quota of electrons to the Mo atom (six from $C_5H_5^-$, two from $CF_3C_2CF_3$, two from CO, four from O^{2-}, and two from $C_6F_5S^-$). Woodward and co-workers have suggested that the acetylene ligand in complex **2** is a four-electron donor, this giving Mo a closed shell of electrons. A closed shell of electrons in complex **3** is also postulated via a triply bonded, six-electron-donor terminal oxide. We note however that the Mo–S bond lengths in these complexes (2.366 (1) Å for complex **2**, 2.403 (2) Å for complex **3**, although longer than in complex **1**, are still significantly shorter than would be expected for an Mo–S single bond (see above). It is possible therefore that in addition to the formulation invoked[17] for **2** and **3**, S→Mo pπ→dπ bonding also plays a part in producing a closed shell of electrons in these complexes.

The Mo–C(carbonyl) distances (1.969 and 1.977 (3) Å) are slightly longer than the corresponding bond lengths in PhB(pz)$_3$Mo(CO)$_2$C$_7$H$_7$[15] (1.938 and 1.946 (5) Å). The dimensions of the *p*-chlorobenzenethiolato moiety (Table II) are unexceptional with S–C = 1.778 (3) Å, Cl–C = 1.746 (4) Å, and mean C–C = 1.373 (5) Å. The conformation of the *p*-chlorobenzenethiolato ligand is such that the Mo–S–C(41)–C(42) torsion angle is 10.4° and the aromatic ring lies between two of the pyrazolyl rings of the HB(Me$_2$pz)$_3$ ligand with N(21)–Mo–S–C(41) and N(31)–Mo–S–C(41) torsion angles of −44.5 and 42.9°, respectively. That this conformation is adopted in the crystal in preference to any other is presumably ascribable to crystal-packing effects.

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Supplementary Material Available: Listings of structure factors, thermal parameters, and hydrogen positional parameters (23 pages). Ordering information is given on any current masthead page.

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Contribution from the Istituto di Chimica Generale e Inorganica,
Università, Istituto CNR, 50132 Florence, Italy

Singlet ⇌ Quintet Spin Transitions of Iron(II) Complexes with a P_4Cl_2 Donor Set. X-ray Structures of the Compound $FeCl_2(Ph_2PCH{=}CHPPh_2)_2$ and of Its Acetone Solvate at 130 and 295 K

F. CECCONI, M. DI VAIRA, S. MIDOLLINI, A. ORLANDINI, and L. SACCONI*

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While the pseudooctahedral compounds FeX$_2$(dppen)$_2$ with a P$_4$X$_2$ donor set (dppen = *cis*-1,2-bis(diphenylphosphino)ethylene; X = Cl, Br) maintain μ_{eff} values close to 5.0 μ_B over the range 90–300 K or exhibit smoothly decreasing μ_{eff} values with decreasing temperature, the corresponding solvates, with formula FeX$_2$(dppen)$_2$·*n*S (X = Cl, S = (CH$_3$)$_2$CO, CH$_2$Cl$_2$, CHCl$_3$; X = Br, S = (CH$_3$)$_2$CO) exhibit abrupt temperature-induced spin transitions in the range 190–230 K between the singlet and quintet ground states. An X-ray structural investigation performed on the compound FeCl$_2$(dppen)$_2$·2(CH$_3$)$_2$CO at 295 K (high-spin isomer, space group $P2_1/a$, a = 17.867 (4) Å, b = 13.089 (4) Å, c = 11.519 (3) Å, β = 93.30 (3)°, Z = 2) and at 130 K (low-spin isomer, poor quality data, a = 17.02 (2) Å, b = 13.02 (2) Å, c = 11.28 (2) Å, β = 94.3 (1)°) has shown that the Fe–P bond distances decrease dramatically (by ca. 0.28, Å in the mean) in the quintet-to-singlet transition. Comparison with the structure of a polymorph of FeCl$_2$(dppen)$_2$ (295 K, high spin, space group $P2_1/n$, a = 16.086 (6) Å, b = 13.189 (6) Å, c = 10.840 (5) Å, β = 90.42 (5)°, Z = 2) indicates that crystal packing and the presence of solvent molecules in the lattice are the factors determining the magnetic properties of these compounds.

Introduction

A previous investigation on pseudooctahedral iron(II) chloride complexes with polyphosphines has shown that they may be either in the singlet ground state if the Fe–P bond lengths are in the normal range or in the quintet ground state if such bonds are abnormally long.[1] The correlation between such bond distances and the nature of the ground state was considered worthy of further investigation. Suitable compounds to this investigation were the iron(II) complex FeCl$_2$(dppen)$_2$ (dppen = *cis*-1,2-bis(diphenylphosphino)ethylene, Ph$_2$PCH=CHPPh$_2$), which has been assigned a trans-octahedral coordination geometry,[2] and its solvates with formula FeCl$_2$(dppen)$_2$·*n*S (S = (CH$_3$)$_2$CO, CH$_2$Cl$_2$, CHCl$_3$), which have been obtained and characterized in this laboratory. The magnetic moment of the unsolvated compound was reported to vary smoothly in the temperature interval 83–353 K.[2] On the contrary, the magnetic moments of the solvated compounds vary abruptly, within a few degrees, from the high-spin to the low-spin values, as the temperature is lowered. Therefore the latter compounds provide the opportunity to

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