Bull Soc Chim Fr (1996) 133, 225-227

Communication

Synthesis and electronic structure of a homoleptic trithiocarbonato iron complex: $[PPh_4]_3[Fe(CS_3)_3]{\bullet}H_2O$

Winfried Plass, Achim Müller*, Erich Krickemeyer, Hartmut Bögge, Ekkehard Diemann

Fakultät für Chemie der Universität, Lehrstuhl für Anorganische Chemie I,
Postfach 100 131, 33501 Bielefeld, Germany

(Received 1 December 1995; accepted 8 March 1996)

Summary — Reaction of iron(III)acetylacetonate with K_2CS_3 in DMF and precipitation with $[PPh_4]Cl$ gives $[PPh_4]_3[Fe(CS_3)_3]{\bullet}H_2O$, the crystal structure of which shows octahedrally-coordinated iron centers within the discrete $[Fe(CS_3)_3]^{3-}$ anions with interesting electronic structure. The CS_3^{2-} group acts as a bidentate ligand with resulting FeS distances ranging from 2.286 to 2.323 Å.

trithiocarbonate / iron complex / X-ray structure / electronic structure

Résumé — **Synthèse et structure électronique d'un complexe de fer trithiocarbonaté homoleptique $[PPh_4]_3[Fe(CS_3)_3]{\bullet}H_2O$.** *La réaction du fer(III)acétylacétonate avec K_2CS_3 dans le DMF et précipitation avec $(PPh_4)Cl$ donne $[PPh_4]_3[Fe(CS_3)_3]{\bullet}H_2O$ dont la structure cristalline montre la coordination octaédrique des atomes de fer dans les anions $[Fe(CS_3)_3]^{3-}$. Le groupe CS_3^{2-} constitue un ligand bidenté avec une liaison de 2,286 à 2,323 Å avec FeS.*

trithiocarbonate / complexe du fer / structure RX / structure électronique

Complexes with sulfur-rich ligands are of current interest for problems of bioinorganic chemistry and research in materials science and catalysis [1, 2]. Trithiocarbonates show activity as antiwear and antioxidant additives to lubricant oils and greases [3]. Surprisingly, only very few structurally-characterized homoleptic transition metal complexes have been reported in the literature [4, 5], probably due to the difficulties in preparing pure compounds, especially single crystals. Here we report the synthesis of $[PPh_4]_3[Fe(CS_3)_3]{\bullet}H_2O$, which was prepared by the reaction of iron(III)acetylacetonate in DMF with potassium trithiocarbonate [6] and precipitation with tetraphenylphosphonium chloride.

The solid state IR spectrum shows the characteristic ν(CS) bands of the bidentate CS_3^{2-} ligands, due to their local C_{2v} symmetry, at 988(vs), 981(m), 936(w), 873(m) and 843(w) cm^{-1} (for details of assignment and a normal coordinate analysis of $[Ni(CS_3)_2]^{2-}$ see [7]). The crystal structure [8] proves the occurrence of the planar $FeS_2C{=}S$ moiety too, and additionally an almost regular octahedral FeS_6 chromophore. The structure of the complex anion $[Fe(CS_3)_3]^{3-}$ is shown in figure 1, with details of the bond distances. It should be mentioned that an octahedrally, rather than a tetrahedrally, S-coordinated Fe(III) center is rather rare.

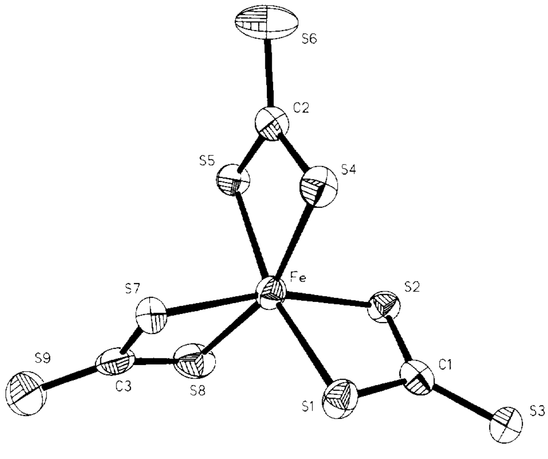

Fig 1. The structure of $[Fe(CS_3)_3]^{3-}$ in crystals of the $[PPh_4]^+$ salt. Selected bond lengths (Å) and angles (°): Fe–S1 2.297(3); Fe–S2 2.323(3); Fe–S4 2.319(3); Fe–S5 2.313(3); Fe–S7 2.286(3); Fe–S8 2.313(3); S1–C1 1.725(8); S2–C1 1.719(8); S3–C1 1.666(9); S4–C2 1.699(8); S5–C2 1.726(8); S6–C2 1.671(9); S7–C3 1.718(9); S8–C3 1.794(11); S9–C3 1.625(9); S1–Fe–S2 74.17(9); S4–Fe–S5 73.56(9); S7–Fe–S8 74.75(10); S1–Fe–S5 166.07(10); S2–Fe–S7 164.36(10); S4–Fe–S8 160.89(10).

---

* Correspondence and reprints

Very interesting is the lattice structure, as the cations represent ca 80% of the lattice volume. This means that the anions may be regarded as guests in the *hydrophobic host lattice* of the large tetraphenylphosphonium cations.

The trithiocarbonato iron(III) complex reported here is the simplest member of a class of iron(III) thio chelates of which the dithiocarbamates are the most thoroughly studied. A series of the latter are well-known examples of spin crossover behavior and exhibit unusual electronic and magnetic properties [9]. The Fe–S bond lengths in the range 2.286–2.323 Å observed in the complex anion $[Fe(CS_3)_3]^{3-}$ agree well with those reported for comparable low-spin iron(III) dithiocarbamate complexes (with an average of 2.31 Å [10]), and therefore indicate a low-spin $^2T_2$ electronic ground state.

The electronic absorption spectra (in DMF solution) exhibit bands (ε in $M^{-1}cm^{-1}$) at 30 800 (8 500), 27 600 (7 000), 22 600 (2 500) and 17 400 cm^{-1} (2 000). The solid state reflectance and transmission spectra (NIR, KBr pellet) basically resemble the solution spectra except for two additional bands at 13 300 (sh) and 11 400 cm^{-1}. The band with the highest energy is due to a ligand internal electronic transition (cf ref [11]). According to the low-spin ground state the band at lowest energy is assigned to the $^2T_2 \rightarrow {}^4T_1$ transition (cf ref [12]). The transition energies and the rather high extinction coefficients of the other bands are basically in line with the observations from the dithiocarbamate (dtc) complexes [12, 13] indicating in the present case a high degree of electron delocalization or metal–ligand orbital mixing. The electron delocalization in $[Fe(CS_3)_3]^{3-}$ is especially high as the π-bonding system has a larger extension than in the dtc complexes (see MO calculations for the CS_3^{2-} anion in [11]). In agreement with the $^2T_2$ electronic ground state assignment, the room temperature ESR spectrum does not show any observable resonances according to relevant fast relaxation [14]. Magnetic measurements for $[PPh_4]_3[Fe(CS_3)_3]{\bullet}H_2O$ in the temperature range 2–300 K clearly show that the low-spin $^2T_2$ state is the electronic ground state with a resulting effective magnetic moment of 1.92 μ_B (see fig 2). Even at room temperature, in contrast to all dtc complexes no evidence is observed for the population of the high-spin $^6A_1$ state. The low-spin ground state is further confirmed by Mössbauer data recorded at 77 K giving an isomer shift $\delta = 0.47 \pm 0.02$ mms^{-1} (vs α-Fe) and a quadrupole splitting $\Delta E_Q = 0.90 \pm 0.02$ mms^{-1} (see fig 3).

Experimental section

All manipulations were carried out under an inert atmosphere of argon using oxygen-free solvents. A solution of iron(III)acetylacetonate (1.41 g, 4 mmol) in DMF (75 mL, dried and distilled prior to use) was mixed within 5 min with 2.80 g (15.0 mmol) potassium trithiocarbonate and stirred for a further 10 min (dark brown solution). After filtration a solution of tetraphenylphosphonium chloride (5.16 g, 13.8 mmol) in 30 mL water was added and the mixture kept in a closed vessel at 5 °C. After 1 week the black crystals were filtered off, washed with water and 2-propanol and dried in an argon stream (yield: 3.5 g, 2.5 mmol).

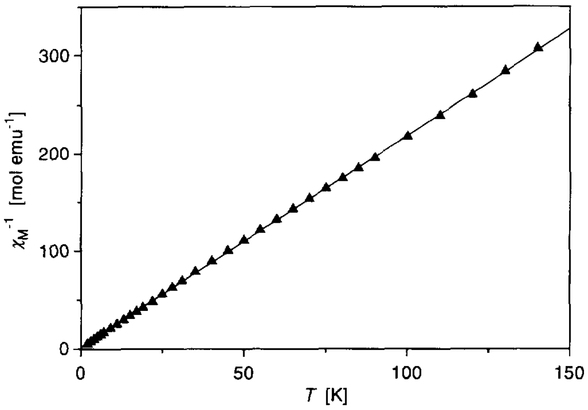

Fig 2. Temperature dependence of the inverse molar susceptibility for $[PPh_4]_3[Fe(CS_3)_3]{\bullet}H_2O$. The solid line represents the fitted Curie–Weiss law with $\Theta = -0.8$ K and a g-value of 2.22 which corresponds to $\mu_{eff} = 1.92\mu_B$.

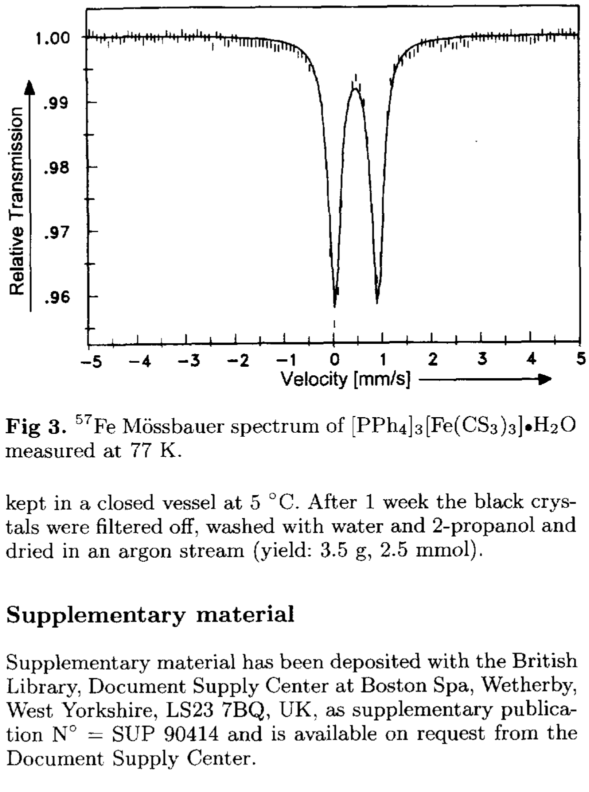

Fig 3. ^{57}Fe Mössbauer spectrum of $[PPh_4]_3[Fe(CS_3)_3]{\bullet}H_2O$ measured at 77 K.

Supplementary material

Supplementary material has been deposited with the British Library, Document Supply Center at Boston Spa, Wetherby, West Yorkshire, LS23 7BQ, UK, as supplementary publication N° = SUP 90414 and is available on request from the Document Supply Center.

Acknowledgment

The financial support of the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. We also thank M Jansen and N Wagner, Bonn, for carrying out the measurement of the susceptibilities and AX Trautwein and M Kröckel, Lübeck, for the measurement of the Mössbauer spectra.

References

1 a) Kuehn CG, Isied SS, *Prog Inorg Chem* (1980) 27, 153
b) Coucouvanis D, *Acc Chem Res* (1981) 14, 201

2 Chianelli RR, Pecoraro TA, Halbert TR, Pan W-H, Stiefel EI, *J Catal* (1984) 86, 226

3 Dumdum JM, Mendelson LT, Pilling RL, *US Patent 4908142 (Chem Abstr* (1990) 112, 201925k)

4 McKechnie JS, Miesel SL, Paul IC, *J Chem Soc, Chem Commun* (1967) 152

5 a) Vicente J, Chicote M-T, González-Herrero P, Jones PG, *J Chem Soc, Chem Commun* (1995) 745
b) Müller A, Krickemeyer E, El-Katri F, Rehder D, Stammler A, Bögge H, Hellweg F, *Z Anorg Allg Chem* (1995) 621, 1160

6 a) Deskin WA, *J Am Chem Soc* (1958) 80, 5680
b) Fackler Jr JP, Coucouvanis D, *J Am Chem Soc* (1966) 88, 3913

7 Cormier A, Nakamoto K, Christophliemk P, Müller A, *Spectrochim Acta* (1974) 30A, 1059

8 Crystal data: $C_{75}H_{62}FeOP_3S_9$, $M = 1416.5$ monoclinic, $C2/c$, $a = 22.576(5)$, $b = 14.240(3)$, $c = 42.557(9)$ Å, $\beta = 98.72(3)°$, $V = 13523(5)$ Å^3, $Z = 8$, λ (Mo-$K\alpha$) = 0.71073 Å, $\mu = 0.618$ mm^{-1}, $D_c = 1.392$ g/cm^3. Data collection ($T = 183$ K): Siemens R3m/V diffractometer, ω scan, refined with SHELXTL Plus V4.11 and SHELXL-93 (GM Sheldrick, University of Göttingen, 1993), Lorentz and polarization corrections, direct methods. The phenyl rings were treated as rigid units (C–C 1.39 Å, C–H 0.96 Å, C–C–C and C–C–H 120°) during the refinement

9 Cotton FA, Wilkinson G, *Advanced Inorganic Chemistry*, Wiley, New York, 5th ed, 1988

10 Orpen AG, Brammer L, Allen FH, Kennard O, Watson DG, Taylor R, *J Chem Soc, Dalton Trans* (1989) S1

11 Müller A, Seidel H, Rittner W, *Spectrochim Acta* (1967) 23A, 1619

12 Lever ABP, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 2nd ed, 1984

13 Ewald AH, Martin RL, Sinn E, White AH, *Inorg Chem* (1969) 8, 1837

14 a) Mabbs FE, Collison D, *Electron Paramagnetic Resonance of d Transition Metal Compounds*, Elsevier, Amsterdam, 1992
b) Bencini A, Gatteschi D, In: *Transition Metal Chemistry, ESR Spectra of Metal Complexes of the First Transition Series in Low-Symmetry Environments*, Melson GA, Figgis BN, Eds, Dekker, New York, 1982, Vol 8, p 1