477–478; m) M. Nazhaoui, J. P. Joly, S. Kitane, M. Berrada, *J. Chem. Soc. Perkin Trans. 1* **1998**, 3845–3850.

[6] a) H. Tsukube, S. Shinoda, J. Uenishi, T. Kanatani, H. Itoh, M. Shiode, T. Iwachido, O. Yonemitsu, *Inorg. Chem.* **1998**, *37*, 1585–1591; b) V. Andrisano, G. Gottarelli, S. Masiero, E. H. Heijne, S. Pieraccini, G. P. Spada, *Angew. Chem.* **1999**, *111*, 2543–2544; *Angew. Chem. Int. Ed.* **1999**, *38*, 2386–2388.

[7] a) P. S. K. Chia, L. F. Lindoy, G. W. Walker, G. W. Everett, *J. Am. Chem. Soc.* **1991**, *113*, 2533–2537; b) P. S. K. Chia, L. F. Lindoy, G. W. Walker, G. W. Everett, *Pure Appl. Chem.* **1993**, *65*, 521–526.

[8] a) J. Lacour, C. Ginglinger, F. Favarger, S. Torche-Haldimann, *Chem. Commun.* **1997**, 2285–2286; b) C. Ginglinger, D. Jeannerat, J. Lacour, S. Jugé, J. Uziel, *Tetrahedron Lett.* **1998**, *39*, 7495–7498; c) J. Lacour, J. J. Jodry, C. Ginglinger, S. Torche-Haldimann, *Angew. Chem.* **1998**, *110*, 2522–2524; *Angew. Chem. Int. Ed.* **1998**, *37*, 2379–2380.

[9] J. Lacour, S. Barchéchath, J. J. Jodry, C. Ginglinger, *Tetrahedron Lett.* **1998**, *39*, 567–570.

[10] a) I. P. Evans, A. Spencer, G. Wilkinson, *J. Chem. Soc. Dalton Trans.* **1973**, 204–209; b) L. F. Cooley, C. E. L. Headford, C. M. Elliot, D. F. Kelley, *J. Am. Chem. Soc.* **1988**, *110*, 6673–6682.

[11] In the absence of TRISPHAT salts, no transfer of color from the aqueous to the organic layer is observed.

[12] a) A. J. McCaffery, S. F. Mason, B. J. Norman, *J. Chem. Soc. (A)* **1969**, 1428–1441; b) M. Ziegler, A. von Zelewsky, *Coord. Chem. Rev.* **1998**, *177*, 257–300.

[13] Chiral discriminations occur among three-bladed propellers. For leading references see: a) J. Breu, K. J. Range, *Monatsh. Chem.* **1994**, *125*, 141–151; b) J. Breu, C. R. A. Catlow, *Inorg. Chem.* **1995**, *34*, 4504–4510; c) H. Sato, A. Yamagishi, S. Kato, *J. Am. Chem. Soc.* **1992**, *114*, 10933–10940; d) A. Yamagishi, Y. Goto, M. Taniguchi, *J. Phys. Chem.* **1996**, *100*, 1827–1832; e) I. Dance, M. Scudder, *J. Chem. Soc. Dalton Trans.* **1998**, 1341–1350; f) J. Breu, A. J. Stoll, *Acta Crystallogr. Sect. C* **1996**, *52*, 1174–1177; g) J. Breu, P. Belser, H. Yersin, *Acta Crystallogr. Sect. C* **1996**, *52*, 858–861.

[14] In the experiments performed with [**3**][Δ-**1**], the signals for the aromatic protons of cation **3** overlap with the signals of the [Ru(diimine)$_3$]$^{2+}$ ions. Our protocol of NMR enantiomeric determination by addition of [**2**][Λ-**1**][8a] cannot be used.

[15] The solutions of [**3**][Δ-**1**] are prepared by dissolution of the salt in DMSO and then dilution with CHCl$_3$.

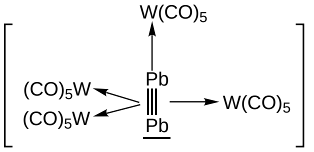
Pb$_2^{2-}$ as Ligand in [Ph$_4$P]$_2$[{W(CO)$_5$}$_4$Pb$_2$]**

Peter Rutsch and Gottfried Huttner*

Dedicated to Professor Hans Brintzinger
on the occasion of his 65th birthday

The heavy element homologues of dinitrogen are only stable at high temperature in the gas phase.[1] In the condensed phase such compounds can be stabilized by coordination to organometallic building blocks.[2, 3] For the element dimers As$_2$, Sb$_2$, and Bi$_2$ the coordination of the diatomic molecules to three side-on-bound 16-valence-electron complex fragments has proven to be particularly appropriate as a method for stabilizing such units.[3] In the cartwheel-shaped compounds [{W(CO)$_5$}$_3$X$_2$] (X = As, Sb, Bi (**2**)) the distances between the main group elements X are only slightly longer than in the free particles X$_2$ (cf. d(Bi–Bi) 2.66 Å in Bi$_{2(g)}$[1] and 2.82 Å in [{W(CO)$_5$}$_3$Bi$_2$][3d]). The three W(CO)$_5$ building blocks, which symmetrically surround the X$_2$ unit in the axis of the molecule, can therefore be considered as an organometallic matrix, within which these units are trapped.

As an isoelectronic analogue of Bi$_2$ it should also be possible to stabilize Pb$_2^{2-}$ in this way.[4] All attempts, however, to construct this fragment, which is also isoelectronic to C$_2^{2-}$, and to integrate it in a stabilizing matrix have thus far been unsuccessful. We report here on **1**, which was synthesized from [K$_2$W$_2$(CO)$_{10}$] and Pb(NO$_3$)$_2$ and was obtained as the tetraphenylphosphonium salt in the form of black, metallic shiny crystals. [(Ph$_4$P)$^+$]$_2$-**1** dissolves in THF to give an intense violet solution, the IR and ^{13}C NMR spectrum of this solution confirm the presence of two types of W(CO)$_5$ units in **1**. Thus, the known compound [{W(CO)$_5$}$_3$Bi$_2$] (**2**) was prepared for comparison.[3d]



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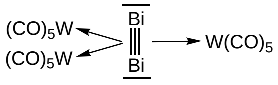

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Compound **2** displays, as expected for a complex with three equivalent W(CO)$_5$ units, the spectroscopic signature of equivalent, coordinatively bound W(CO)$_5$ groups with a sharp band at 2054 cm^{-1} and a broad, intense absorption at 1963 cm^{-1}. The ν_{CO} band pattern in **1** is considerably more complex and its overall appearance and, in particular, the two shortwave bands at 2057 and 2034 cm^{-1} which display a ratio of intensities of 1:3, indicates that two different sets of W(CO)$_5$ groups are present in **1**. The anionic character of **1** is evident in a shift of the center of the $\tilde{\nu}_{CO}$ bands from 1980 cm^{-1} in the neutral compound **2** to 1928 cm^{-1} in **1**. The ^{13}C NMR spectrum of **1** shows an intense signal at $\delta = 202.9$ that has both ^{207}Pb and ^{183}W satellites ($^2J_{Pb,C} = 34$, $^1J_{W,C} = 124$ Hz). This signal is assigned to the equatorial carbonyl groups. The signal for the axial carbonyl groups of the side-on-coordinated W(CO)$_5$ units ($^2J_{Pb,C} = 26$ Hz) appears at $\delta = 206.5$. The weaker signal of the axial carbonyl group of the terminal W(CO)$_5$ unit occurs at $\delta = 208.4$ ($^2J_{Pb,C} = 20$, $^1J_{W,C} = 126$ Hz). The ratio of intensities and the positions of the signals support the given assigments. The fundamental similarity betweeen the bonding in **1** and **2** mirrors itself in the UV/Vis spectra. The longwave absorption of **2** (570 nm, $\varepsilon = 11\,700\,\text{M}^{-1}\text{cm}^{-1}$) corresponds to an absorption of **1** at 583 nm ($\varepsilon = 4500\,\text{M}^{-1}\text{cm}^{-1}$); the prominent absorptions at shorter wavelengths (428 nm ($\varepsilon = 12200\,\text{M}^{-1}\text{cm}^{-1}$) in **2**; 415 nm ($\varepsilon = 6600\,\text{M}^{-1}\text{cm}^{-1}$) in **1**) as well as the shoulders (340 nm ($\varepsilon = 13\,000\,\text{M}^{-1}\text{cm}^{-1}$) in **2**; 320 nm ($\varepsilon = 21\,000\,\text{M}^{-1}\text{cm}^{-1}$) in **1**) also correspond. These bands lie in a region, which is characteristic for Bi$_2$ or the isoelectronic PbTe in the gas phase.[1] The

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structure of **1** was determined for crystals of the salt $[(Ph_4P)^+]_2$-**1** at 233 K.[5]

Compound **1** contains a dumbbell-shaped Pb_2 unit, which is surrounded in a cartwheel-like fashion by three $W(CO)_5$ units (W_b, Figure 1) and which carries a further $W(CO)_5$ group on one end (Pb1, W_a). The Pb–W distance to the terminally bound $W(CO)_5$ group is 287 pm, the Pb–W distances to the tungsten centers of the side-on-bound units are significantly longer (325 pm).[7] These unusually long bond lengths correspond to the likewise unusually long Bi–W distances in **2** (311 pm). The distance between the two lead centers in the axis of the molecule of **1** is only 281 pm. It is the shortest known Pb–Pb distance.[6] This finding is consistent with the interpretation of the Pb_2 unit in **1** as Pb_2^{2-}, which is stabilized by coordination to $W(CO)_5$ units. The Bi–Bi distances in $Bi_{2(g)}$ (266 pm)[1] and in **2** (282 pm)[3d] can be considered as a basis for the Pb–Pb distance expected in Pb_2^{2-}. In view of the lower nuclear charge of Pb in comparison to that of Bi, and in view of the two negative charges in **1**, the Pb–Pb distance in Pb_2^{2-} should be longer than the Bi–Bi distance in the isoelectronic $Bi_{2(g)}$. The observed value of 281 pm for **1** meets this expectation and shows in comparison with the corresponding value of **2** the electronic similiarity between Pb_2^{2-} and Bi_2 in the complexes **1** and **2**, respectively. The terminal coordination of an additional $W(CO)_5$ group in **1** reveals that Pb_2^{2-} can function as an end-on-coordinating Lewis base.

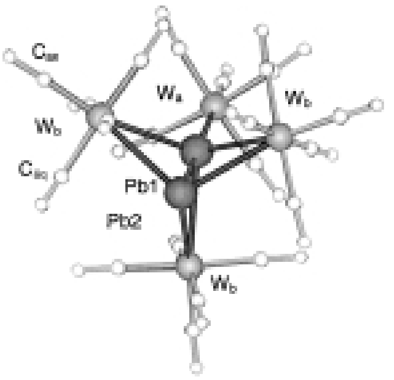

Figure 1. Structure of **1** in the crystal of $[(Ph_4P)^+]_2$-**1**.[6] Selected bond lengths [pm] and angles [°]: Pb1-Pb2 280.6(8), Pb1-W_a 287.1(8), Pb1-W_b 333.9(1), 326.3(9), 325.1(1), Pb2-W_b 320.2(1), 322.1(5), 322.0(1), W_b-C_{eq} 194.2(1)-204.1(3), W_a-C_{eq} 201.2(1)-205.3(1), W_b-C_{ax} 193.6(1)-195.6(1), W_a-C_{ax} 198.1(1); W_a-Pb1-Pb2 178.1(9),Pb1-W_b-Pb2 50.8(2)-51.4(2), W_b-Pb1-Pb2 62.1(2)-63.7(2), W_b-Pb2-Pb1 64.9(2)-67.1(2), W_a-Pb1-W_b 114.8(3)-117.9(3), W_b-Pb1-W_b 99.1(3)-103.4(3), W_b-Pb2-W_b 100.7(2)-107.3(3).

Experimental Section

Synthesis of $[Ph_4P]_2[\{W(CO)_5\}_4Pb_2]$ $[(Ph_4P)^+]_2$-**1** (experimental conditions see ref. [8]; C,H analyses: Mikroanalytisches Laboratorium, Organisch-chemisches Institut der Universität Heidelberg): $[W(CO)_6]$ (1755 mg, 5 mmol) was added to a suspension of KC_8 (1350 mg, 10 mmol) in THF (200 mL).[8, 9] The colorless mixture was stirred for 6 h at room temperature. It changed color progressively from yellow to yellow-brown to brown; the initially strong evolution of CO ceased with time. Filtration through Kieselgur gave a brown solution, from which $[K_2W_2(CO)_{10}]$ (760 mg, 1.04 mmol; 42%) precipitated as a yellow-orange powder, after concentration to 10 mL and addition of diethyl ether (100 mL). The identity of the product was deduced from a comparison of its IR spectrum with that of pure $[Na_2W_2(CO)_{10}]$.[10] For the preparation of **1**, $[K_2W_2(CO)_{10}]$ was not isolated, but the suspension was used directly, which according to the stoichiometry and yield still contained unconverted KC_8. $Pb(NO_3)_2$ (2 g, 6 mmol) was added to the reaction mixture, which was then stirred for a further 36 h under exclusion of light. Filtration of the black suspension through Kieselgur (5 cm) and concetration to 3 mL afforded a violet oil, which was purified by chromatography on silica gel (15 cm). After separation of $[W(CO)_6]$ and other $W(CO)_5$-containing compounds with THF, the dipotassium salt of **1** was eluted with ethanol as a deep violet band. After concentration to 5 mL, a solution of Ph_4PCl (1110 mg, 3 mmol) in EtOH (5 mL) was added, which led to the precipitation of $[(Ph_4P)^+]_2$-**1** in the form of black crystal flakes. After careful decanting the residue was dissolved in THF (≈3 mL), layered with ethanol, and left to crystallize. After 5 d $[(Ph_4P)^+]_2$-**1** (450 mg, 0.19 mmol; 38% yield, based on $[K_2W_2(CO)_{10}]$) was obtained in the form of black, metallic shiny crystals. ^{1}H NMR: $\delta = 7.97-7.79$ (m, 40H; H_{arom}); ^{13}C NMR: $\delta = 208.4$ (m, $^2J_{C,Pb} = 20$ Hz, $^1J_{C,W} = 126$ Hz, 1C; C_{ax}), 206.5 (t, $^2J_{C,Pb} = 26$ Hz, 3C; C_{ax}), 202.9 (m, $^2J_{C,Pb} = 34$, $^1J_{C,W} = 124$ Hz, 16C; C_{eq}), 135.8–118.4 (m, 48C; C_{arom}); ^{31}P NMR: $\delta = 24.1$ (s, 2P; Ph_4P); IR (THF): $\tilde{\nu}(CO) = 2057$ (w), 2034 (s), 2013 (vs), 1997 (vs), 1915 (br), 1869 (sh), 1858 cm^{-1} (sh); UV/Vis (THF): $\lambda_{max}(\varepsilon) = 320$ (21000), 415 (6600), 583 nm (4500 $M^{-1}cm^{-1}$); elemental analysis (%): calcd: C 34.19, H 1.68; found: C 33.88, H 2.08.

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[1] K. P. Huber, G. Herzberg in *Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules, Vol. 4*, Van Nostrand Reinhold Company, New York, **1979**.

[2] C. F. Campana, A. Vizi-Orosz, G. Palyi, L. Markó, L. F. Dahl, *Inorg. Chem.* **1979**, *18*, 3054–3059.

[3] a) B. Sigwarth, L. Zsolnai, H. Berke, G. Huttner, *J. Organomet. Chem.* **1982**, *226*, C5–C8; b) B. Sigwarth, O. Scheidsteger, L. Zsolnai, O. Orama, G. Huttner, *Organometallics* **1985**, *4*, 326–332; c) O. Scheidsteger, B. Sigwarth, U. Weber, G. Huttner, *Angew. Chem.* **1982**, *94*, 210–211; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 411; d) U. Weber, L. Zsolnai, G. Huttner, *Z. Naturforsch. B* **1982**, *37*, 707–710.

[4] The bond dissociation energy of Pb_2^{2-} is not known. The experimentally determined sequence of dissociation energies of Pb_2 (8 valence electrons, 0.8 eV), PbBi (9 valence electrons, 1.4 eV), and BiBi (10 valence electrons, 2.0 eV) suggests that Pb_2^{2-} with 10 valence electrons should be comparably stable. For details on the properties of diatomic molecules see ref. [1].

[5] At lower temperatures the crystals of $[(Ph_4P)^+]_2$-**1** decompose with retention of their habitus to give an X-ray amorphous powder (for the structure of $[(Ph_4P)^+]_2$-**1** see ref. [6]).

[6] Crystal structure data: The X-ray structure analysis was carried out on a Nonius-Kappa-CCD diffractometer with $Mo_{K\alpha}$ radiation ($\lambda_{Mo} = 0.71074$ Å). Data collection and reduction was performed with the Nonius Software COLLECT.[11] The SHELXTL-PLUS software package was used for the structure solution and refinement. The structures were solved by direct methods with SHELXS-86 and refined with SHELXL-93.[12] The program XPMA was used for the graphical workup of the data.[13] The figure was generated with WINRAY-32.[14] The refinement was carried out anisotropically against F^2, hydrogen atoms were included in calculated positions. Structure data for **1**: space group $P\bar{1}$, $a = 12.343(3)$, $b = 12.806(3)$, $c = 24.605(5)$ Å, $\alpha = 96.69(3)$, $\beta = 96.94(3)$, $\gamma = 110.85(3)°$, $V = 3554 \times 10^6$ pm^3, $\rho_{calcd} = 2.232$ g cm^{-3}, $2\theta_{max} = 61.8°$, $Z = 2$, 41927 measured reflections, 21593 independent reflections, of which 12537 were observed ($I > 2\sigma(I)$), 868 refined parameters, $R = 0.051$, $Rw = 0.113$, residual electron density $\leq 4.39 \times 10^{-6}$ e pm^{-3}. (An overview of more than 250 X-ray crystallographically determined Pb–Pb distances is found in the database of the Cambridge Crystallographic Data Centre (status 1999): F. H. Allen, J. E. Davis, J. J. Galloy, O. Johnson, O. Kennard, C. F. Macrae, E. M. Mitchell, G. F. Mitchell, J. M. Smith, D. G. Watson, *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187–204.) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-141592. Copies of the data can be obtained free of charge on

application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[7] The distances to Pb1, which bears the terminal W(CO)$_5$ group, are all slightly longer than the W$_b$–Pb2 distances to the non-terminally coordinated Pb center (see Figure 1).

[8] P. Kircher, G. Huttner, K. Heinze, *J. Organomet. Chem.* **1998**, *562*, 217–227.

[9] a) M. A. Schwindt, T. Lejon, L. S. Hegedus, *Organometallics* **1990**, *9*, 2814–2819; b) J. Maher, R. Beatty, R. Cooper, *Organometallics* **1985**, *4*, 1354–1361; c) J. Ellis, S. Hentges, D. Kalina, G. Hagen, *J. Organomet. Chem.* **1975**, *97*, 79–93.

[10] E. Lindner, H. Behrens, S. Birkle, *J. Organomet. Chem.* **1968**, *15*, 165–175.

[11] COLLECT, software for data collection, Nonius, **1998**; http://www.nonius.com.

[12] a) G. M. Sheldrick, SHELXS-86, Program for Crystal Structure Solution, Universität Göttingen, **1986**; b) G. M. Sheldrick, SHELXL-93, Program for Crystal Structure Refinement, Universität Göttingen, **1993**; http://www.shelx.uni-ac.gwdg.de/shelx/index.html; c) *International Tables for X-Ray Crystallography, Vol. 4*, Kynoch, Birmingham, **1974**.

[13] L. Zsolnai, G. Huttner, XPMA, Universität Heidelberg, **1998**; http://www.rzuser.uni-heidelberg.de/~v54/xpm.html.

[14] R.Soltek, G. Huttner, WINRAY-32, Universität Heidelberg, **1998**; http://www.rzuser.uni-heidelberg.de/~v54.

Strong Field Iron(II) Complex Converted by Light into a Long-Lived High-Spin State**

Franz Renz,* Hiroki Oshio, Vadim Ksenofontov, Markus Waldeck, Hartmut Spiering, and Philipp Gütlich*

Octahedral coordination compounds of transition metal ions with a d^4 to d^7 electronic configuration can be classified according to the ligand-field strength (LFS) into three groups: 1) low-spin (LS) state (strong LFS); 2) high-spin (HS) state (weak LFS), and 3) thermal spin crossover between HS ↔ LS (intermediate LFS), for example in the case of iron(II) complexes with a HS($^5T_{2g}$) ↔ LS($^1A_{1g}$) transition.[1]

More than ten years ago, the surprising observation was made that thermally switchable Fe^{II} spin-crossover complexes can also be optically switched from the LS to the HS state (LIESST = light-induced excited spin-state trapping“[2, 1a]) and from the HS to the LS state (reverse LIESST[1a]).

Usually, LS Fe^{II} complexes decay after photoexcitation within nanoseconds from the metastable HS state back to the LS state.[3] Herein, we report on an entirely unexpected observation: Complex molecules of $[Fe(tpy)_2]^{2+}$ (tpy = 2,2′:6′,2″-terpyridine) embedded at a 2% concentration in the host matrix of the corresponding manganese compound $[Fe_{0.02}Mn_{0.98}(tpy)_2](ClO_4)_2$ (**1**) exhibit LS behaviour at room temperature, yet may be converted by light to the HS state with an effectively infinite lifetime (low-temperature tunneling lifetime $t^0_{HL} > 10^5$ s) at 10 K (LIESST effect).

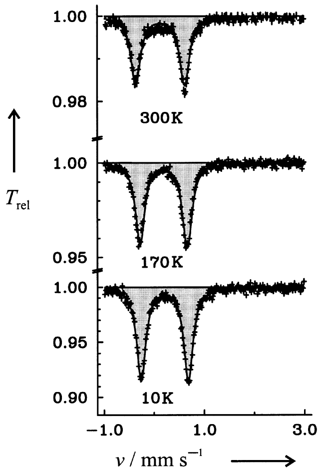

Figure 1. Mössbauer spectra of **1** at 300, 170, and 10 K. The spectra indicate only one quadrupole doublet, which is typical for Fe^{II} in the LS state.

The compounds **1** and $[Fe(tpy)_2](ClO_4)_2$ (**2**) were prepared by literature methods.[4a, 5] The Mössbauer spectra[4b] of **1** (Figure 1) and **2** exhibit LS behavior at ambient and lower temperatures ($^1A_{1g,}$ ground state). The spectra of **1** at 300, 170, and 10 K each exhibits a quadrupole doublet of isomer shift values ($\delta = 0.13$, 0.20, 0.22 mm s^{-1}) and quadrupole splitting values ($\Delta E_Q = 0.98$, 0.95, 0.98 mm s^{-1}), respectively. These values are typical for LS Fe^{II}.[6]

Figure 2 shows the Mössbauer spectrum of **1** recorded after 30 min irradiation with green light at 10 and 80 K. At 10 K the spectrum now contains two quadrupole doublets: one ($\delta = 0.22$ mm s^{-1}, $\Delta E_Q = 0.97$ mm s^{-1}) originates from the original LS ground state; the other ($\delta = 0.95$ mm s^{-1}, $\Delta E_Q = 2.08$ mm s^{-1}) is indicative of Fe^{II} in the HS state (LIESST).[6] Presuming the Lamb–Mössbauer factors for the LS and HS states are equal, the fraction of $[^{57}Fe(tpy)_2]^{2+}$ complex molecules converted by light to the long-lived LIESST state is 66%, as estimated from the area fraction of the HS doublet. The spectrum recorded at 80 K (Figure 2) shows only the quadrupole doublet ($\delta = 0.21$ mm s^{-1}, $\Delta E_Q = 0.94$ mm s^{-1}) of the original LS ground state. This observation—which shows that the light-induced metastable HS state has relaxed back to the LS state—was fully reproducible. No light-induced spin-state conversion was observed for compound **2**, the pure iron compound.

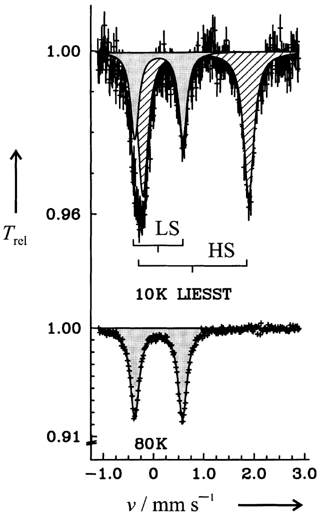

Figure 2. Mössbauer spectrum of compound **1** after irradiation with green light at 10 K. Comparison with Figure 1 shows that the major fraction has been converted to the HS state. After heating to 80 K, the Mössbauer spectrum indicated only the LS state remained.

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