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Mössbauer Spectra of Some Bis(N,N-disubstituted dithiocarbamato)iron(III) Compounds

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Mössbauer spectra were obtained on several iron(III) complexes of the general formula $(R_2NCS_2)_2FeX$, where X represents Cl, Br, I, NCS, or $C_6F_5CO_2$. There was no systematic variation in the isomer shifts which were all close to 0.64 mm/sec (with respect to sodium nitroprusside) at room temperature. The quadrupole splitting ranged from 2.4 to 3.0 mm/sec and showed systematic variation with X with little or no dependence on R.

Introduction

Iron(III) with five d electrons can theoretically exist in a doublet ("low-spin"), quartet, or sextet ("high-spin") spin ground state in its complexes. A quartet ground state is, however, theoretically impossible if the iron(III) is in a crystal field of cubic symmetry.[1] Both doublet and sextet states are common in the cubic case.

The first well-authenticated type of iron(III) complex with iron in a spin quartet ground state, halobis(N,N-dialkyldithiocarbamato)iron(III), was reported only in 1966,[2] although such a ground state had been suggested for chloro(phthalocyanine)iron(III) as early as 1959.[3] The phthalocyanine complex has received insufficient investigation to establish its spin character unambiguously. It is perhaps significant that both of these complexes have five-coordinated iron(III) in a square- (C_{4v}) or rectangular- (C_{2v}) pyramidal configuration, a crystal field far removed from octahedral symmetry.

Most interest has been shown in the halobis(dialkyldithiocarbamato)iron(III) complexes, as evidenced by the number of papers which have appeared in the period of less than 2 years since the original report.[4-8] The crystal structure of $Fe(S_2CN(C_2H_5)_2)_2Cl$[2] and the magnetic susceptibilities[4] and esr[4,5] and Mössbauer spectra[4-7] of $Fe(S_2CN(CH_3)_2)_2Cl$, $Fe(S_2CN(C_2H_5)_2)_2Cl$, $Fe(S_2CN(i\text{-}C_3H_7)_2)_2Cl$, and $Fe(S_2CN(C_2H_5)_2)_2Br$ have been determined.

Experimental Section

Most of the chlorides, bromides, and iodides used in the present investigation were prepared in the usual method by treating a benzene solution of tris(N,N-disubstituted dithiocarbamato)iron(III) with concentrated aqueous hydrochloric, hydrobromic, and hydriodic acids.[2,8] The resulting green-black precipitates were collected and washed well, first with anhydrous ethanol to remove excess acid and then with benzene. Drying was carried out under vacuum over refluxing water for several hours. Recrystallization was generally not undertaken because analytically pure compounds resulted in most cases from this procedure. Also, many were insufficiently soluble in nonreacting solvents.

Thiocyanate derivatives were prepared by using a solution of sodium thiocyanate in dilute aqueous sulfuric acid in place of the aqueous hydrohalic acid. The following is a typical preparation. Two grams (0.025 mol) of sodium thiocyanate was dissolved in a cold mixture of 1.5 ml (0.027 mol) of concentrated sulfuric acid in 10 ml of water and this solution was added to 75 ml of a saturated benzene solution of tris(3-azabicyclo[3.2.2]nonane-N-carbodithioato)iron(III). After 1 min or so of vigorous stirring (the reaction time was kept as short as possible because considerable red ferric thiocyanate complex is formed upon longer stirring), the precipitate was collected, washed with absolute ethanol until the washings, initially reddish owing to the Fe–SCN complex, were pale greenish or almost colorless, then washed with benzene, and finally dried as above.

Some reactions with carboxylic acids were investigated. These involved acetic, benzoic, monochloroacetic, dichloroacetic, trifluoroacetic, and pentafluorobenzoic acids and were only of an exploratory nature. The ease of formation of a green color in the initially brown benzene solutions of the tris complexes upon heating varied directly with the strength of the acid and decreased in the order: C_6F_5COOH, $CF_3COOH > CHCl_2COOH > CH_2ClCOOH \gg CH_3COOH$, C_6H_5COOH. Acetic and benzoic acids caused no color change even upon a few hours of reflux. Only in one case to date has a pure product been isolated. It appears certain that many more carboxylate complexes (at least of the strong acids trifluoroacetic, pentafluorobenzoic, dichloroacetic, etc.) could be prepared when optimum reaction conditions have been determined.

Preparation of Pentafluorobenzoatobis(3-azabicyclo[3.2.2]-nonane-N-carbodithioato)iron(III).—A solution of 1.3 g (0.0020 mol) of tris(3-azabicyclo[3.2.2]nonane-N-carbodithioato)iron(III) and 0.86 g (0.0040 mol) of pentafluorobenzoic acid in 25 ml of benzene was refluxed 1 hr, cooled to room temperature, filtered, and evaporated to dryness under vacuum at room temperature. The residue was redissolved in 25 ml of benzene, the solution was filtered, and the complex was reprecipitated by addition of pentane. The precipitate was washed well with ether and dried under vacuum 12 hr at room temperature.

Elemental analyses (performed by Galbraith Laboratories, Knoxville, Tenn.) were obtained on 13 representative bis dithiocarbamates. The identity and purity (*i.e.*, lack of contamination with the corresponding tris dithiocarbamate complex) were checked for the unanalyzed compounds by a comparison of their electronic spectra with the electronic spectra of the analytically pure compounds. *Anal.* Calcd for $FeC_6H_{12}N_2S_4Cl$ [Fe(ME)$_2$Cl]: Cl, 10.7. Found Cl, 11.0. Calcd for $FeC_6H_{12}N_2S_4Br$ [Fe(ME)$_2$Br]: Br, 21.2. Found: Br, 21.0. Calcd for $FeC_6H_{12}N_2S_4I$ [Fe(ME)$_2$I]: I, 30.3. Found: I, 30.7. Calcd for $FeC_7H_{12}N_3S_5$ [Fe(ME)$_2$SCN]: C, 23.7; H, 3.39;

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[1] J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, London, 1961, p 366.

[2] B. F. Hoskins, R. L. Martin, and A. H. White, *Nature*, **211**, 627 (1966).

[3] J. S. Griffith, *Discussions Faraday Soc.*, **26**, 81 (1959).

[4] H. H. Wickman, A. M. Trozzolo, H. J. Williams, G. W. Hull, and F. R. Merritt, *Phys. Rev.*, **155**, 563 (1966).

[5] H. H. Wickman and F. R. Merritt, *Chem. Phys. Letters*, **1**, 117 (1967).

[6] H. H. Wickman and A. M. Trozzolo, *Inorg. Chem.*, **7**, 63 (1968).

[7] H. H. Wickman and A. M. Trozzolo, *Phys. Rev. Letters*, **16**, 162 (1966).

[8] R. L. Martin and A. H. White, *Inorg. Chem.*, **6**, 712 (1967).

TABLE I

ROOM-TEMPERATURE QUADRUPOLE SPLITTINGS (MM/SEC) FOR $(R_2NCS_2)_2FeX$

Dithiocarbamate ligand	X^- ligand				
	$C_6H_5COO^-$	SCN^-	Cl^-	Br^-	I^-
ME		2.56	2.67	2.86	2.96
ET		2.55	2.63	2.78	2.87
HMI		2.52	2.68	2.86	3.04
AZA	2.46	2.63	2.56	2.84	2.91
CHX			2.68	2.84	2.86
PYR		2.40[a]	2.64	2.76	2.95
PIP		2.58	2.61	2.81	2.88
Average	2.46	2.56 ± 0.03	2.64 ± 0.03	2.82 ± 0.03	2.92 ± 0.05

[a] Not averaged.

N, 11.9. Found: C, 25.0; H, 3.57; N, 11.5. Calcd for $FeC_{10}H_{20}N_2S_4Br$ [Fe(ET)$_2$Br]: C, 27.8; H, 4.66; Br, 18.5. Found: C, 28.9; H, 4.76; Br, 18.7. Calcd for $FeC_{10}H_{20}N_2S_4I$ [Fe(ET)$_2$I]: I, 26.5. Found: I, 26.7. Calcd for $FeC_{14}H_{24}N_2S_4Cl$ [Fe(HMI)$_2$Cl]: Cl, 8.06. Found: Cl, 7.82. Calcd for $FeC_{14}H_{24}N_2S_4Br$ [Fe(HMI)$_2$Br]: Br, 16.5. Found: Br, 16.8. Calcd for $FeC_{14}H_{24}N_2S_4I$ [Fe(HMI)$_2$I]: I, 23.9. Found: I, 24.3. Calcd for $FeC_{26}H_{44}N_2S_4Br$ [Fe(CHX)$_2$Br]: Br, 12.3. Found: Br, 12.7. Calcd for $FeC_{18}H_{28}N_2S_4Br$ [Fe(AZA)$_2$Br]: Br, 14.9. Found: Br, 15.0. Calcd for $FeC_{19}H_{28}N_3S_5$ [Fe(AZA)$_2$SCN]: C, 44.4; H, 5.48; N, 8.17. Found: C, 44.2; H, 5.40; N, 8.40. Calcd for $FeC_{25}H_{28}N_2S_4O_2F_5$ [Fe(AZA)$_2$PFB]: C, 45.0; H, 4.23, N, 4.20. Found: C, 46.0; H, 4.24; N, 3.92. Abbreviations used: ME, $(CH_3)_2NCS_2^-$; ET, $(C_2H_5)_2NCS_2^-$; HMI, $C_6H_{12}NCS_2^-$; CHX, $(C_6H_{11})_2NCS_2^-$; AZA, 3-azabicyclo[3.2.2]nonanecarbodithioate, $C_8H_{14}NCS_2^-$; PFB, $C_6F_5CO_2^-$.

Electronic and infrared spectral data were obtained on Cary Model 14 and Beckman Model 1R-8 recording spectrophotometers, respectively.

Mössbauer spectra were obtained using a constant-acceleration drive in the time mode and a 400-channel analyzer. Velocity scale calibration and the isomer shift reference point were obtained by frequent measurements of sodium nitroprusside. Peak position and approximate line widths were read from the oscilloscope or from a plot of the data.

Results and Discussion

Electronic Spectral Data.—The electronic spectrum (in the range 700–230 mμ) was recorded for the methylene chloride solutions of the bis(N,N-disubstituted dithiocarbamato)iron(III) complexes prepared in this study. The spectra are quite complex: at least six peaks, some of which appear as ill-defined shoulders (especially the peak at 485–510 mμ), occur in the visible region. These peaks are very intense and must be due to charge-transfer processes. Any d–d transitions which might occur in this region cannot be observed.

Some interesting regularities are observed when the peak positions of each series are compared. The ranges in mμ of the positions of the first four peaks are: for Cl, 621–623, ~487, 438–446, 371–379; for Br, 609–614, ~500, 444–452, 384–392; for I, 596–602, 505–512, 452–458, 373–378; for SCN, 615–617, ~510, 437–438, 375–379. The iodo complexes are characterized by a peak in the range 420–427 mμ, which is completely absent in all of the other complexes, and the bromo complexes are characterized by a flat peak in the range 332–357 mμ, which is actually a poorly resolved doublet. Although it is impossible at present to make a definite electronic assignment to each of the peaks, owing to both the complexity of the spectra and the fact that the peaks are charge transfer, it is possible to use electronic spectral data to determine halide or thiocyanate substitution. The positions of the peaks depend on the halide or thiocyanate and are almost completely independent of the nitrogen substituent in the dithiocarbamate.

There is a peak at 2050–2060 cm^{-1}, due to C–N stretching, in the infrared spectra of the thiocyanate complexes in methylene chloride solution. It has been suggested that values below 2100 cm^{-1} indicate the thiocyanate is nitrogen bonded to the metal;[9] however, this does not appear to be always the case. It is impossible to determine unequivocally from the position of the C–N stretch whether the thiocyanate is nitrogen or sulfur bonded to the iron. Thus, no significance should be attached to our use of SCN for complexed thiocyanate.

Mössbauer Spectral Data.—The room-temperature results given in Table I are sufficient for this discussion. (When several compounds were examined at liquid nitrogen temperature, the isomer shift increased by 0.10 mm/sec, a normal temperature shift, and the quadrupole splittings were unchanged.) The experimental error in the quadrupole splittings listed in Table I was estimated to be ±0.03 mm/sec on the bases of replicate measurements.

The values of the splittings are arranged in Table I according to both the nitrogen substituent on the dithiocarbamate and the fifth ligand X^- in the general formula $(R_2NCS_2)_2FeX$. Generally for any given R, the splitting increases from left to right, as the X^- ligands are arranged. Any description then of the bonding must account for the ordering of the X^- ligands shown. For any given X^-, there is apparently no trend with R, and so we may average over the R's to obtain the average splitting characteristic of the group X^-.

Despite the general trends noted, there remain the following anomalies. (1) In the AZA series there is a reversal of splitting values for the chloride and thiocyanate. These values were confirmed by repeated measurements and also by repeated syntheses and

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[9] I. Bertini and A. Sabatini, *Inorg. Chem.*, **5**, 1025 (1966).

appear to be real. (2) Although point-charge considerations suggest that the Cl^-–Br^- difference and the Br^-–I^- difference should be about the same, in most cases the Cl^-–Br^- difference was considerably greater. (3) Finally, although much similarity is anticipated in the ME and ET series, the latter has definitely smaller splittings for the Br^- and I^-. The explanation of these anomalies will not be attempted in this paper but will require more detailed analysis.

The isomer shift values were independent of either R or X. For any given R the average deviation was essentially the experimental error, ±0.01 mm/sec. The average isomer shift for all compounds was 0.64 ± 0.02 mm/sec (relative to sodium nitroprusside).

Although the origin of the splitting has not been worked out theoretically, we can assume that there is a very large, constant valence contribution (about 3 mm/sec), which, in view of the very asymmetric environment, is temperature independent, as well as independent of small geometric differences between compounds. We may then inquire as to the lattice contribution considering the five nearest ligand atoms as point charges. Agreement with the observed results will be obtained by considering the principal component of the EFG[10] (due primarily to the valence contribution) to be positive and directed along the Fe–X axis. The four sulfur atoms forming the base of the pyramid form a rectangle (not a square) and generate an asymmetry parameter, η, in the EFG. The point-charge estimate of this is $\sim$0.2 in reasonable agreement with that deduced by Wickman and Trozzolo[6] from the low-temperature resolved hyperfine spectrum of a typical bis dithiocarbamate. Because the observed splitting varies as $[1 + (\eta^2/3)]^{1/2}$, typical values of η around 0.2 have practically no effect on the simple doublet spectrum, and any effects due to changes in ligand (which could affect η *via* the SFeS angle) go unobserved. The contribution due to X^-, however, being negative and along the major axis, is subtracted directly from the valence contribution and is readily observed. As X^- gets effectively closer to Fe, its contribution increases, and so the splitting decreases regularly from I^- to Br^-, etc., the order being the same as the spectrochemical series.

The magnitude of the difference from one halogen to another can be estimated using a point-charge approximation. The Fe–Cl distance is known and we assume that the Br^- and I^- distances are greater by amounts corresponding to their greater ionic radii. Thus the difference in splitting between chloride and iodide is predicted to be 0.36 mm/sec while the average measured difference in the seven pairs of compounds (with different R's) came to 0.30 mm/sec.

If we had not postulated a large valence EFG and considered only the point charges, we would have predicted rather small splittings.

The spectra of several compounds displayed relaxation broadening of the lower energy peak (even at room temperature in some cases). In hemin and related complexes, which have a square-pyramidal structure, relaxation broadening of the higher energy peak has been commonly observed and has been associated with a positive V_{zz}. However, Wickman and Trozzolo[6] found from the Mössbauer hyperfine spectra of four different bis dithiocarbamates that the magnetization axis was perpendicular to the principal EFG axis. Hence the broadening of the lower energy line is consistent with a positive V_{zz} in these cases.

Finally, consider the constancy of the isomer shifts. One might be tempted, on the basis of the large isomer shift values and their constancy, to call the compounds ionic, but this view is contrary to (a) the intense visible spectra with dominance of charge transfer and (b) the iron–halide and iron–sulfur distances (which in $Fe(ET)_2Cl$ are $\sim$0.2 Å shorter than the ionic values). The isomer shifts are distinctly more positive than the hemins, an effect which could be ascribed to increased d-electron shielding. Note that for the spin quartet state there is an empty d orbital, and partial occupancy of this *via* π bonding with the ligands will increase the shielding effect and hence the isomer shift. The constancy of the isomer shift with varying X suggests that π bonding with X is not an important contribution. We are attempting to make compounds with $X^- = F^-$ and CN^- in order to test the foregoing suggestion on ligands with extremes of π-bonding character.

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[10] Electron field gradient.