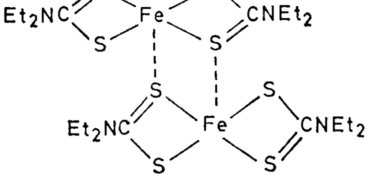
Magnetic and Mössbauer Investigations of *NN*-Disubstituted Bis(dithiocarbamato)iron(II) Complexes

By **Brian W. Fitzsimmons,*** Department of Chemistry, Birkbeck College (University of London), Malet Street, London WC1E 7HX
Saad E. Al-Mukhtar, Leslie F. Larkworthy, and **Ramesh R. Patel,** The Joseph Kenyon Laboratory, University of Surrey, Guildford GU2 5XH

Bis(dithiocarbamato)iron(II) complexes [$\{Fe(S_2CNR_2)_2\}_n$] have been found to form two classes. With R = Et, Pr^n, or Bu^n, isomorphous relations with copper(II) complexes of known structure show that the complexes are dimers containing square-pyramidal iron. Considerable antiferromagnetic interaction is present, and the chemical isomer shifts and reflectance spectra are characteristic of high-spin Fe^{II}. Very large quadrupole splittings (*ca.* 4.2 mm s^{-1}) have been obtained. These complexes exhibit clean quadrupole doublets at 4.2 K consistent with diamagnetic ground states as expected for dimers. This is confirmed by the behaviour in an applied field. When R = Me or R$_2$ = C_4H_8 no isomorphous relations have been found, but polymeric octahedral structures are suggested by the smaller quadrupole splitting (*ca.* 2.5 mm s^{-1}), weaker antiferromagnetism, reflectance spectra indicating less distortion, and the complex magnetic-hyperfine splitting at 4.2 K in zero field.

THIS paper reports the preparation and investigation of bis(*NN*-dialkyldithiocarbamato)iron(II) complexes, [$\{Fe(S_2CNR_2)_2\}$] (R = Me, Et, Pr^n, Bu^n, and R$_2$ = C_4H_8). While tris(dithiocarbamato)iron(III) complexes are well known because of the spin isomerism [1] which occurs in many of them, and the complexes [$Fe(S_2CNR_2)_2X$] (X = halogen or NO) have been extensively investigated [2] because of their square-pyramidal structure and associated properties, very little information [2,3] is available concerning the very air-sensitive Fe^{II} complexes. The complex [$\{Fe(S_2CNEt_2)_2\}_2$] has been shown [4] to be isomorphous with [$\{Cu(S_2CNEt_2)_2\}_2$] which is known [5] to be an axially bridged five-co-ordinate dimer; presumably the Fe^{II} complex has a similar structure, (I). Some Fe^{II} complexes of this type have been used as reactive intermediates [6] without definite identification; while the present work [7] was being carried out, the Mössbauer parameters of several iron(II) dithiocarbamates were reported,[8,9] but no magnetic susceptibility determinations, reflectance spectra, or further *X*-ray powder investigations were described.



(I)

EXPERIMENTAL

Solvents were deoxygenated before use and all operations were carried out under nitrogen with apparatus similar to that described earlier.[10] The bis(dithiocarbamato)iron(II) complexes (Table 1) were precipitated on addition of

TABLE 1

Analyses (%) [a] and reflectance spectra

Complex	Colour	Analyses				ν (cm^{-1}) [b]	
		C	H	N	Fe	Charge transfer [c]	$^5T_{2g} \rightarrow {}^5E_g$
[$\{Fe(S_2CNMe_2)_2\}_n$]	Yellow	24.1	4.0	8.75	19.2	23 000 (sh), 18 700 (sh), 16 700 (sh)	8 600m, 6 200s
		(24.3)	(4.1)	(9.5)	(18.8)	[23 500 (sh), 18 700 (sh), 16 700 (sh)]	[8 800m, 6 500s]
[$\{Fe(S_2CNEt_2)_2\}_2$]	Chocolate	34.5	5.8	6.9	16.0	19 400 (sh)	9 500m
		(34.1)	(5.7)	(8.0)	(15.8)	[20 600 (sh)]	[9 900m, 5 800w [d]]
[$\{Fe(S_2CNPr^n{}_2)_2\}_2$]	Chocolate	41.15	6.9	7.0	13.3	22 500 (sh), 19 400 (sh), 16 800 (sh)	9 800m, 5 900w
		(41.15)	(6.9)	(6.9)	(13.7)	[22 200 (sh), 19 200 (sh), 16 700 (sh)]	[10 400m, 5 700w]
[$\{Fe(S_2NBu^n{}_2)_2\}_2$]	Yellow-brown	46.05	7.7	5.9	12.3	22 500 (sh), 19 300 (sh), 16 800 (sh)	9 400 b
		(46.5)	(7.8)	(6.05)	(12.0)	[22 700 (sh)]	[9 600b]
[$\{Fe(S_2CNC_4H_8)_2\}_n$]	Yellow	34.6	4.5	8.1	16.35	23 200 (sh), 18 600 (sh), 16 700 (sh)	8 400m, 6 000s
		(34.5)	(4.6)	(8.1)	(16.0)	[22 400 (sh), 19 900 (sh), 16 700 (sh)] 18 600 (sh)	[8 500m, 6 400s]

[a] Calculated values are given in parentheses. [b] At room temperature; values at liquid-nitrogen temperature are given in square brackets. [c] These shoulders are on the side of very broad multicomponent absorptions rising to much higher frequencies. [d] Not clearly visible at room temperature.

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aqueous iron(II) sulphate to an aqueous solution of the sodium dithiocarbamate. The solids were filtered off, washed several times with distilled water, dried by pumping continuously on them for *ca.* 10 h, and were then sealed *in vacuo* in Pyrex tubes. Several of the suspensions were very slow to filter. The dibutyldithiocarbamate complex was washed several times by decantation with water, dried, then transferred to the filter in a nitrogen bag, and washed with distilled water several times before being finally dried. The complexes are much more susceptible to aerial oxidation when wet. They were analysed for iron by direct ignition to Fe_2O_3.

Physical Measurements.—Magnetic measurements were carried out down to liquid-nitrogen temperature by the Gouy method, at several field strengths to ensure that ferromagnetic impurities were absent. Reflectance spectra were recorded at room and liquid-nitrogen temperature on a Unicam SP 700C spectrophotometer. Mössbauer spectra in applied magnetic fields were obtained by the P.C.M.U., Harwell. Spectra at 80 K were measured using a conventional constant acceleration spectrometer. *X*-Ray powder photographs were recorded with a Philips camera PW1024/00 of radius 116.6 mm and copper K_α radiation. In all cases precautions were taken to exclude air, and measurements were carried out on samples in tubes or cells sealed *in vacuo* or under nitrogen.

RESULTS AND DISCUSSION

Reflectance Spectra.—Octahedral high-spin Fe^{II} complexes are expected [11] to show one weak spin-allowed *d–d* transition, $^5T_{2g} \rightarrow {}^5E_g$, in the near-i.r. region, but usually distortion from octahedral symmetry causes one very broad and asymmetric band or two bands to appear. The dithiocarbamatoiron(II) complexes fall into the latter category (Table 1), indicating considerable distortion, greater when R = Et and Pr^n where the band separation was *ca.* 4 000 cm^{-1} than with R = Me and $R_2 = C_4H_8$ where it was *ca.* 2 000 cm^{-1}. The relative intensities of the bands were reversed in the two sets of complexes, and the lower-frequency band in the spectrum of the di-n-butyl complex was so weak that it was obscured by ligand bands. The resemblance to the spectra of octahedral Fe^{II} complexes indicates that these bis(chelate) complexes have polymeric structures. It is suggested below that when R = Et, Pr^n, and Bu^n the complexes are dimers with approximately square-pyramidal co-ordination, and when R = Me and $R_2 = C_4H_8$ the complexes are octahedral polymers. This is consistent with the smaller band separation in the spectra of the latter class. Monomeric tetrahedral structures are excluded by the fact that Fe^{II} present in a tetrahedral ZnS lattice absorbs [12] at *ca.* 3 500 cm^{-1}.

The absorptions in the 9 000 cm^{-1} region were weak by reflectance which is perhaps why none was detected [9] for samples of $[\{Fe(S_2CNEt_2)_2\}_2]$ and $[\{Fe(S_2CNPr^n{}_2)_2\}_2]$ in KBr discs, although weak bands were occasionally found in the disc spectrum of $[\{Fe(S_2CNMe_2)_2\}_n]$ at 9 400 and 6 600 cm^{-1}, in reasonable agreement with our values. The reflectance spectra of some corresponding zinc(II) complexes exhibited intense absorption rising steeply from *ca.* 24 000 cm^{-1} so that the shoulders (Table 1) on the intense ligand absorption can be assigned to charge-transfer processes.

Magnetic Properties.—A high-spin Fe^{II} complex in regular octahedral configuration ($^5T_{2g}$ ground term) is expected to have a magnetic moment at room temperature well above the spin-only value of 4.90 B.M. because of considerable orbital contribution.* The moment is not expected to be much reduced or to vary over the accessible temperature range even when distortion and delocalisation effects are included.[13] The large variation with temperature of the magnetic moments (Tables 2 and 3) of the iron(II) dithiocarbamates must therefore be due to antiferromagnetism. Substitution of the values of *g* and *J* [$J = -7.6$, $g = 2.13$ (R = Me); $J = -16.7$, $g -2.15$ (Et); and $J = -4.2$ cm^{-1}, $g = 1.97$ ($R_2 = C_4H_8$)] in the expression for magnetic interaction in a binuclear molecule with $S = 2$ approximately reproduced the magnetic behaviour of these complexes but unrealistically high *g* values ($g \approx 2.5$, $J \approx -20$ cm^{-1}) were required when R = Pr^n or Bu^n to obtain even moderate agreement, indicating, as do the room-temperature moments, that considerable orbital contribution was still present. No special significance should be ascribed to the *J* and *g* values except that the temperature variation of moment can be considered to arise from interaction in highly distorted high-spin species.

TABLE 2

Magnetic and Mössbauer data

	$\mu_{eff.}$/B.M.		θ	10^6 Diamagnetic correction [a]	δ [b]	ΔE [b]
Complex	295	89 K	°C	c.g.s. units	mm s^{-1}	
$[\{Fe(S_2CNMe_2)_2\}_n]$	4.84	3.97	78	142	1.00	2.56
$[\{Fe(S_2CNEt_2)_2\}_2]$ [c]	4.42	2.78		190	0.875	4.19
$[\{Fe(S_2CNPr^n{}_2)_2\}_2]$ [c]	5.25	3.49		237	0.87	4.20
$[\{Fe(S_2CNBu^n{}_2)_2\}_2]$ [c]	5.02	2.79		285	1.01	3.93
$[\{Fe(S_2CNC_4H_8)_2\}]$	4.66	4.16	38	176	1.01	2.27

[a] The Curie–Weiss law was used as $\chi_a \propto 1/(T + \theta)$; the Me and C_4H_8 complexes obeyed this law but the remaining complexes had Néel points at 110 (R = Et), 185 (Pr^n), and below 85 K (Bu^n). [b] Isomer shifts, δ, and quadrupole splittings, Δ*E*, at liquid-nitrogen temperature. The isomer shifts are given with respect to natural iron.

Magnetic data are not sufficiently sensitive to degree of polymerisation to allow distinction [14] between dimers and linear polymers. Experimentally, however, the complexes fall into two classes: those which obeyed the Curie–Weiss law with (Table 2) large θ values (R = Me and $R_2 = C_4H_8$), and those for which Néel points were found (R = Et, Pr^n, and Bu^n) in the plots of reciprocal susceptibility against absolute temperature. These

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* 1 B.M. ≈ 9.27×10^{-24} A m^2.

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plots are not of the shape usually found when spin isomerism, also excluded by Mössbauer data, is present.

TABLE 3

Variation with absolute temperature of atomic susceptibilities χ_a (c.g.s. units) and effective magnetic moments $\mu_{eff.}$ (B.M.)

$[\{Fe(S_2CNMe_2)_2\}_n]$								
T/K	295.2	262.5	230.0	198.5	166.3	135.0	103.0	89.0
$10^6\chi_a$	9 845	10 940	11 940	13 460	15 100	17 380	20 290	21 920
$\mu_{eff.}$	4.84	4.81	4.71	4.64	4.50	4.35	4.11	3.97
$[\{Fe(S_2CNEt_2)_2\}_2]$								
T/K	295.2	262.5	230.3	198.5	166.5	135.0	103.0	89.5
$10^6\chi_a$	8 201	8 645	9 225	9 729	10 330	10 640	10 790	10 680
$\mu_{eff.}$	4.42	4.28	4.14	3.95	3.73	3.40	3.00	2.78
$[\{Fe(S_2CNPr^n_2)_2\}_2]$								
T/K	294.9	262.5	230.0	198.4	166.0	135.3	89.5	
$10^6\chi_a$	10 560	10 830	10 950	11 130	11 090	10 990	10 780	
$\mu_{eff.}$	5.02	4.79	4.51	4.22	3.88	3.46	2.79	
$[\{Fe(S_2CNBu^n_2)_2\}_2]$								
T/K	294.5	262.3	230.0	198.3	166.3	135.3	103.5	89.0
$10^6\chi_a$	11 510	12 290	13 050	14 030	14 850	15 850	16 890	16 970
$\mu_{eff.}$	5.25	5.09	4.98	4.73	4.46	4.16	3.75	3.49
$[\{Fe(S_2CNC_4H_8)_2\}_n]$								
T/K	295.2	262.5	232.0	198.0	166.3	135.3	103.0	89.5
$10^6\chi_a$	9 128	10 060	11 230	12 850	14 960	17 880	21 620	23 960
$\mu_{eff.}$	4.66	4.62	4.58	4.53	4.48	4.42	4.24	4.16

Mössbauer Investigations.—Mössbauer spectra were measured at 80 and 4.2 K. External magnetic fields were applied in appropriate cases at 4.2 K. All 80 K spectra comprised clean quadrupole doublets indicating that neither oxidation nor hydrolysis had taken place in course of preparation or during transfer to the spectrometer. The conventional Mössbauer parameters are given in Table 2. The first point to be made is that the chemical isomer shifts are consistent with high-spin Fe^{II} at all temperatures in agreement with the paramagnetic susceptibility measurements. These two lines of evidence exclude the alternative possibilities of spin isomerism between high- and low- or intermediate-spin ($S = 1$) Fe^{II} or the presence of low-spin Fe^{II} alone. To date, low-spin or spin-isomeric $Fe^{II}S_6$ complexes have not been reported. It is evident that, as expected, the crystal-field splitting is too small in the case of the less-charged Fe^{II} for spin pairing to take place. From the mean positions of the *d–d* absorptions (Table 1), Δ for Fe^{II} is *ca.* 8 000 cm^{-1}, well below the value at the cross-over point for Fe^{II} which from the Tanabe–Sugano diagram for d^6 must be at least twice this value.

As with many high-spin Fe^{II} complexes, appreciable quadrupole splittings were observed. This is due to a valence contribution to the total electric-field gradient (e.f.g.) generated by the extra electron over the half-filled *d* shell. For such complexes, the splittings of *ca.* 4 mm s^{-1} are among the largest recorded. This quadrupole splitting is sensitive to the substituent R in the dithiocarbamate ligands. When R = Me or $R_2 = C_4H_8$, the quadrupole splitting was smaller (*ca.* 2.5 mm s^{-1}) than for the Et, Pr^n, and Bu^n complexes which had splittings of *ca.* 4 mm s^{-1}. This quadrupole-splitting difference can be correlated with structure as we confirmed the Et derivative to be isomorphous with the copper(II) analogue (Table 4) which is known to be an axially bridged dimer [5] involving a five-co-ordinate metal as in (I). It is also clear from the *X*-ray powder photographs that the dimeric [2] $[\{Cu(S_2CNPr^n_2)_2\}_2]$ and $[\{Fe(S_2CNPr^n_2)_2\}_2]$ are isomorphous. Large quadrupole splittings are therefore associated with the axially bridged dimeric structure. This structure leads to strong intramolecular antiferromagnetic coupling which is reflected in the paramagnetic susceptibility measurements. The exchange integrals, *J*, from the susceptibility measurements for the dimers, are of the order of 20 cm^{-1} so all the molecules will be in the $S' = 0$ state at 4.2 K. That the ground state is truly non-magnetic was

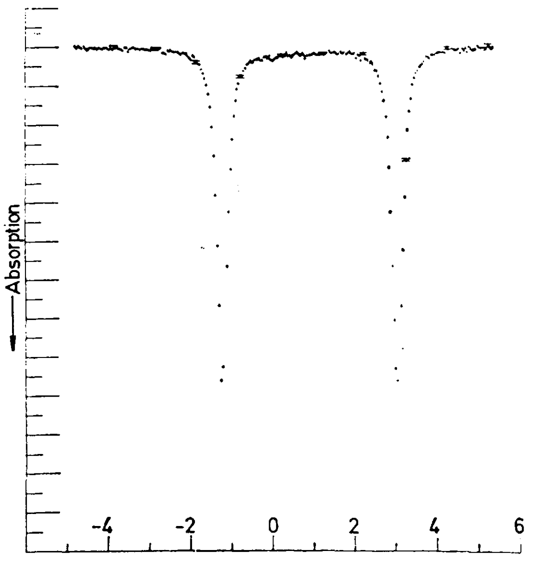

FIGURE 1 Mössbauer spectrum of $[\{Fe(S_2CNEt_2)_2\}_2]$ at 4 K

TABLE 4

X-Ray powder data[a] (d spacings) for the complexes $[\{Fe(S_2CNR_2)_2\}_n]$

R :	Me	Et[b]		Pr^n		Bu^n	C_4H_8
		Fe	Cu	Fe	Cu		
	7.73vs	8.62s	8.76s	10.15s	10.22s	11.20s	9.30vs
	7.08s	7.56s	7.60s	9.18w	8.99m	8.20m	7.63s
	5.46s	7.12s	7.18s	7.76s	7.90m	7.08m	5.83s
					7.31m		
	4.43vw	6.05s	6.15s	6.71w	6.83w	5.68w	4.75s
	3.91m	5.01m	5.20vw	5.81w	5.76w	5.27vw	3.96s
	3.13m	4.84m	4.88m	5.18w	5.15w	4.44m	3.31s
	2.96s	4.57m	4.57m	4.70m	4.46w	4.07s	2.92s
	2.78vw	4.35m	4.34m	3.96m	3.96m	3.86vw	2.73m
	2.59w	4.16s	4.21s	3.67s	3.65m	3.68w	2.34s
	2.45m	3.58s	3.70s	3.38m			
	2.33m			3.07w	3.06s		

[a] Estimated visual intensities; copper K_α radiation. [b] The d spacings agree well with those reported in ref. 4.

confirmed by measuring the Mössbauer spectrum in an applied magnetic field at 4.2 K. The spectrum for the Et derivatives (δ 0.895 and ΔE 4.25 mm s^{-1}) is shown in Figure 2. The effective field is small and is just the applied field indicating that the internal field is zero. Antiferromagnetic dimers may be reasonably well characterised, therefore, by combined magnetic and Mössbauer studies. Non-magnetic ground states have been confirmed in this way for the Pr^n (δ 0.79 and ΔE 4.26 mm s^{-1}) and Bu^n (δ 0.89 and ΔE 4.00 mm s^{-1}) derivatives as their magnetically perturbed Mössbauer spectra were similar in all respects to that shown in Figure 2 for the Et complex.

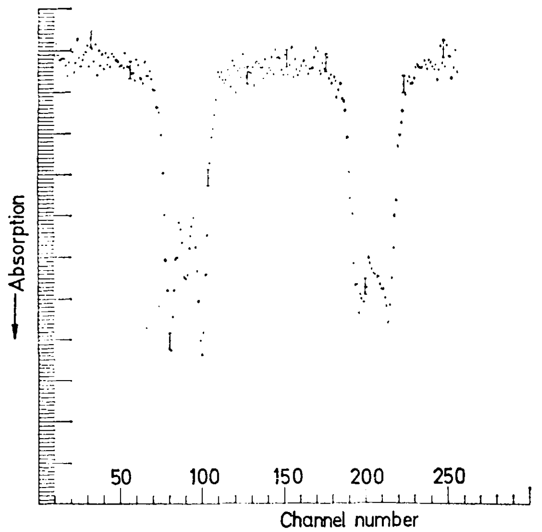

FIGURE 2 Mössbauer spectrum of $[\{Fe(S_2CNEt_2)_2\}_2]$ in an applied perpendicular magnetic field of strength 3.0 T

The Me and the C_4H_8 complexes have structures different from the dimeric series. Paramagnetic susceptibility measurements show metal–metal interaction but it is much lower than in the complexes considered to be dimers. The observed quadrupole splittings are lower than those of the established antiferromagnetic dimers with the axially bridged five-co-ordinate structure. It will be shown that the high quadrupole splittings observed for the dimers arise from reinforcement of the valence contribution by an appreciable lattice contribution. In octahedral high-spin Fe^{II} complexes the lattice and valence contributions normally oppose one another and the observed quadrupole splittings seldom exceed 3 mm s^{-1}. We conclude that the fall in quadrupole splitting from 4.19 observed for the five-co-ordinate Et derivative to 2.27—2.56 mm s^{-1} observed for the Me and C_4H_8 derivatives is caused by a change in structure from five- to six-co-ordinate, the latter being attained by *cis* polymerisation. The Mössbauer spectra at 4.2 K showed a magnetic hyperfine splitting in zero applied field (see Figure 3) so the ground states of these molecules are magnetic. This evidence points strongly to octahedral co-ordination about the metal, necessitating more extensive polymerisation than in the dimers. These hyperfine spectra are similar to the low-temperature spectra of simple Fe^{II} salts. The appearance of more than six Zeeman lines indicates

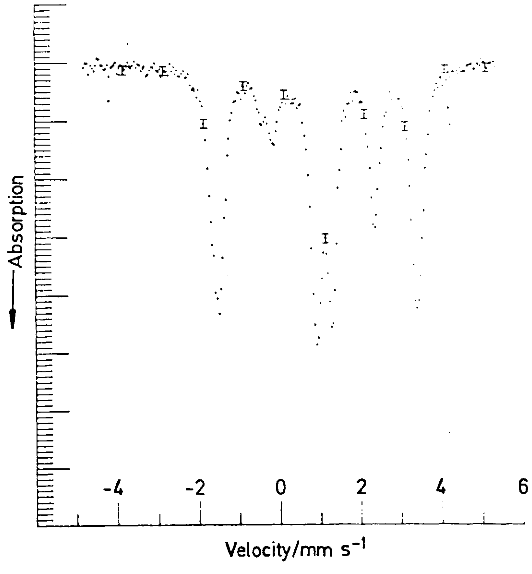

FIGURE 3 Mössbauer spectrum of $[\{Fe(S_2CNMe_2)_2\}_n]$ at 4.2 K in zero applied field

that the magnetic sub-levels are no longer pure $|m_z\rangle$ eigenstates so that the $\Delta m = \pm 2$ transitions are weakly allowed.[15] Although many polymeric $M^{II}S_6$ systems are known, no isomorphous relations were found between the X-ray powder patterns of the complexes $[\{Fe(S_2CNMe_2)_2\}_n]$ and $[\{Fe(S_2CNC_4H_8)_2\}_n]$ and their Cu^{II} and Zn^{II} analogues which could have been more amenable to detailed X-ray investigation than the very air-sensitive Fe^{II} complexes.

Parallel arguments to these have been advanced by de Vries *et al.*[9] who also drew support from their preparation of several anionic complexes such as $[Ph_4P][Fe(S_2CNEt_2)_3]$ which they found had a quadrupole splitting of *ca.* 2.26 mm s^{-1} compared with the values of *ca.* 4 mm s^{-1} found for the five-co-ordinate species. These workers also reported that their samples of $[\{Fe(S_2CNMe_2)_2\}_n]$ contained variable amounts of Fe^{II} in five-co-ordinate as well as octahedral sites as judged from the ΔE values (4.10 and 2.53 mm s^{-1} respectively), whereas our samples appeared to consist almost entirely of the octahedral type but with perceptible absorption at the higher ΔE values indicating that the high-quadrupole-splitting component was present to the extent of 5%. The Et, Pr^n, and Bu^n complexes, as might be expected for dimers as opposed to polymers, are slightly more soluble in organic solvents than the Me and C_4H_8 complexes. Extraction of the Me complex under nitrogen gave a small amount of more soluble material, but this, and the residue, gave the same ΔE of 2.56 mm s^{-1}. Since essentially similar preparative methods were used, this difference is not understood.

We turn now to our observation of positive V_{zz}, the principal component of the e.f.g. for the dimeric complexes. All examples we studied showed the same sign. This positive sign was predicted on the basis of Hückel calculations carried out by de Vries *et al.*[8] who advanced a level scheme of the type

$$(d_{x^2-y^2})^2 \quad (d_{zx},d_{zy})^2 \quad (d_{z^2})^1 \quad (d_{xy})^1$$

for these dimeric molecules. The presence of the sixth electron in a $d_{x^2-y^2}$ orbital brings a strong positive contribution to V_{zz}, whilst the tetragonal perturbation generated by the square-pyramidal geometry contributes positively to V_{zz} also. The iron(II) bis(dithiocarbamates) constitute a case wherein the lattice and valence contributions to V_{zz} act in the same sense.

We thank Mr. M. W. O'Donoghue for recording the X-ray powder photographs of several Cu^{II} and Zn^{II} complexes, The University of Mosul, Iraq, for the award of a scholarship (to S. E. Al-M), the S.R.C. for support, and the staff of the P.C.M.U. at Harwell for measurement of the low-temperature Mössbauer spectra.

[5/110 *Received, 17th January,* 1975]

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