

Complexes of N, S donor ligands. Co^{II} , Co^{III} , Mn^{III} , Fe^{III} and Pd^{II} complexes of 1,2-di(*o*-aminophenylthio)ethane: Synthesis, characterisation and reactions

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MS received 6 April 1992; revised 29 August 1992

Abstract. The ligand 1,2-di(*o*-aminophenylthio)ethane (abbreviated as H_2DAPTE) has been allowed to react with various metal salts and the complexes isolated and characterised. In these complexes, H_2DAPTE behaves as a neutral quadridentate and also as a dibasic quadridentate ligand after losing two protons from the amine functions. Two complexes of this ligand, reported earlier, have been condensed with acetone to form macrocyclic complexes of TDDH where TDDH is 13,13,15-trimethyl-2,5-dithia-12,16-diazatricyclo-[15,3,0,0,6,11]-docosa-1(17),6(11),7,9,15,18,20-heptene.

Keywords. Diamino-dithioether; macrocycle; Curtis reaction.

1. Introduction

There has been continuing interest in the coordination chemistry of both open-chain and macrocyclic quadridentate ligands containing the N_2S_2 donor set (Petering *et al* 1964; Constable *et al* 1986; Akbar Ali *et al* 1987; Hay *et al* 1987). $\text{Cu}(\text{II})$ complexes of these types of ligands are of considerable importance because of the occurrence of CuN_2S_2 chromophore in blue-copper proteins such as plastocyanin (Hay 1984; Karlin and Zubieta 1983). Macrocyclic complexes of the ligands containing both imine and thioether donors have also been prepared and studied (Thompson and Busch 1964; Elder *et al* 1968; Mukherjee *et al* 1987). These complexes were isolated by reacting Schiff base complexes having thiol donors with bifunctional alkylating agents and thereby generating thioether *in situ*. Another route for synthesising these complexes is the reaction of mono- or diketones with metal complexes of diamino-dithioether ligands by the Curtis reaction (Curtis and House 1961; Curtis 1968). $\text{Ni}(\text{II})$ macrocyclic complexes produced by such reaction with N_2S_2 donors have been reported (Urbach and Busch 1973; Hay *et al* 1976). The Curtis reaction has also been extended to the synthesis of metal complexes with open-chain ligands (Tulchinsky *et al* 1990).

We attempted such reactions with complexes of ligands having metal ions other than $\text{Ni}(\text{II})$. We have chosen 1,2-di(*o*-aminophenyl-thio)ethane, abbreviated as

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H₂DAPTE, as the diamino-dithioether ligand. Molybdenum, tungsten, cobalt and rhodium complexes of this ligand have appeared in the literature (Cannon *et al* 1967; Levason *et al* 1977; Levason and Oates 1978; McAuliffe *et al* 1978).

Metal complexes of H₂DAPTE and their reactions with mono and diketones are reported in this paper. In some cases, deprotonation from two amine functions of H₂DAPTE occurs as is reported for *o*-phenylenediamine complexes (Ricciardi *et al* 1991). The Fe(III) complex, [Fe(H₂DAPTE)Cl₂]Cl, has been reported by us (Mukherjee *et al* 1988).

2. Materials and methods

2.1 Physical measurements

C, H and N analyses of the compounds were carried out in a Perkin-Elmer model 240C elemental analyser. Elemental analyses of the metals were done by conventional methods after decomposing the compounds with concentrated mineral acids. IR spectra were recorded on a Perkin-Elmer model 783 IR spectrophotometer as KBr pellets. Electronic spectra were recorded on a Pye-Unicam SP8-150 spectrophotometer. Conductivity measurements were made with a Philips PR-9500 conductivity bridge and magnetic susceptibility measurements with a Princeton Applied Research model 155 vibrating sample magnetometer. Molecular weights were determined with a Knauer vapour pressure osmometer. Mössbauer spectra were recorded using a 2 × 256 channel multiscalar confined to constant acceleration drive system. The source used was 6 mci ⁵⁷Co in Rh-matrix.

2.2 Preparation

2.2a *The ligand*: H₂DAPTE was prepared by following the method described in the literature (Cannon *et al* 1967).

2.2b *The metal complexes*: The complexes of Cu(II) and Co(II) of the ligand were prepared by refluxing mixtures of equimolar solutions of the ligand and the corresponding metal chloride in EtOH for about 8 h; Na₂PdCl₄ was used for preparing the palladium(II) complex. The complexes separated out either on cooling the solution at room temperature or on refrigeration overnight. The resultant precipitates were recrystallised from EtOH when the desired complexes were obtained in microcrystalline form. The following compounds have been isolated by the above general procedure:

[Co(H₂DAPTE)Cl₂]·H₂O (1) : Brownish purple in colour (yield ≈ 65%)

[Cu₂(H₂DAPTE)₂Cl₃]Cl (2) : Blue in colour (yield ≈ 70%)

[Pd₂(H₂DAPTE)Cl₄] (3) : Yellow in colour (yield ≈ 85%)

Co(III), Mn(III) and Fe(III) complexes were isolated by the following procedure.

[Co(H₂DAPTE)Cl₂]Cl (4) and [Mn(DAPTE)acac] (5) were prepared by adding a methanolic solution of the metal *tris*-acetylacetonate (1 mol) to a boiling solution of the ligand (1 mol) in the same solvent and refluxing the mixture for about half an hour. About 1 cm³ of conc. HCl was then added to the mixture (pH lowered to 3–4)

and it was refluxed for a further period of 6 h and then filtered hot. On keeping the concentrated filtrate overnight, the compounds precipitated out. They were recrystallised from MeOH. The Fe(III) complex, $[\text{Fe}_2(\text{DAPTE})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ (6), was readily obtained by refluxing equimolar ethanolic solutions of the ligand and $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ for about 8 h and on cooling the solution. The product was recrystallised from EtOH. The Co(III) complex was blue, the Mn(III) complex brown and the Fe(III) complex green in colour. The yield in each case was about 70%.

The macrocyclic complexes of Ni(II) and Fe(III), viz. $[\text{Ni}(\text{TDDH})\text{Cl}_2]$ (7) and $[\text{Fe}(\text{TDDH})\text{Cl}_2]\text{Cl}$ (8), respectively, were obtained by the following procedure.

The starting materials for the macrocycles were $[\text{Ni}(\text{H}_2\text{DAPTE})\text{Cl}_2]$ and $[\text{Fe}(\text{H}_2\text{DAPTE})\text{Cl}_2]\text{Cl}$ which were prepared *in situ* through the reaction of $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ and FeCl_3 with the ligand. Methanolic solutions of each of these two components were stirred separately for about half an hour and then excess (about 10 times the required amount) of dry Me_2CO was added dropwise with stirring. The stirring was continued for about 36 h after the addition of Me_2CO . The mixture was then filtered and kept overnight in the refrigerator, when the macrocyclic complexes deposited as microcrystals. They were recrystallised from EtOH. The nickel compound formed blue crystals (yield about 40%) and the ferric compound formed brown crystals (yield about 35%).

3. Results and discussion

3.1 Synthesis and reactivities

Under the conditions of the reactions as employed during the present work, the ligand H_2DAPTE (see figure 1) reacts with different metal salts to form different types of metal complexes (see scheme 1). In the complexes (1)–(4), the ligand behaves as a neutral quadridentate one, but in the complexes (5) and (6) it acts as a dibasic anion after losing two protons from two amine functions. The complexes $[\text{Ni}(\text{H}_2\text{DAPTE})\text{Cl}_2]$ and $[\text{Fe}(\text{H}_2\text{DAPTE})\text{Cl}_2]\text{Cl}$ undergo condensation with acetone to form the macrocyclic complexes of the ligand of *cis*- N_2S_2 type, viz. 13,13,15-trimethyl-2,5-dithia-12,16-diazatricyclo [15, 3, 0, 0, 6, 11]-docosa-1(17), 6(11), 7, 9, 15, 18, 20-heptene, which is abbreviated as TDDH (see scheme 2). The compositions of the resultant macrocycles are $[\text{Ni}(\text{TDDH})\text{Cl}_2]$ (7) and $[\text{Fe}(\text{TDDH})\text{Cl}_2]\text{Cl}$ (8), respectively. The other metal complexes of the ligand did not react with acetone. On investigation, complexes (2) and (3) were found to be binuclear species, the former being bridged through chlorine between the two copper(II) centres and the latter being a complex in which the two amine functions are *trans* to each other. Complexes (5) and (6) contain the ligand in a dibasic anionic form, two protons being lost from two amine functions, so that no reaction occurs with carbonyl groups. For the Co(II) complex

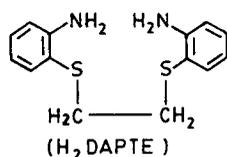
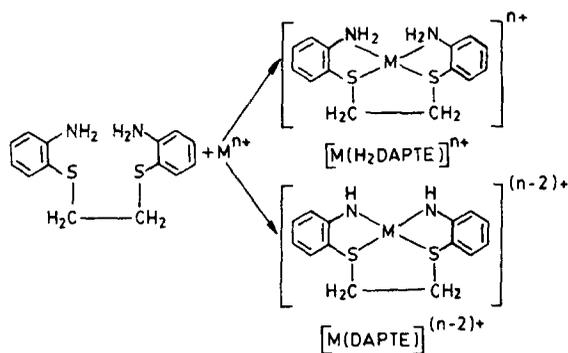
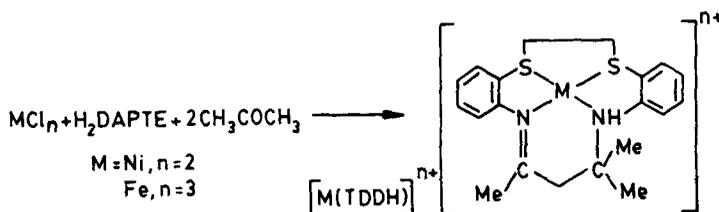


Figure 1. Structure of the ligand 1,2-di(*o*-aminophenylthio)ethane.



Scheme 1.



Scheme 2.

(1), this reaction does not take place, probably due to the distorted octahedral geometry of the complex, as it is a common observation that cobalt(II) complexes do not normally take up square-planar or pure octahedral geometry. Hence, it is difficult for such complexes to form the macrocyclic species whose donor atoms are in square-planar array. The same argument holds for the cobalt(III) complexes (4). Complexes $[\text{Ni}(\text{H}_2\text{DAPTE})\text{Cl}_2]$ and $[\text{Fe}(\text{H}_2\text{DAPTE})\text{Cl}_2]\text{Cl}$ do not react with other dicarbonyls such as diacetyl or acetylacetonone, the reasons for which are not clear.

The copper(II) complex (2) shows characteristics which can be related to model systems for 'blue' or type-I copper proteins. It may be mentioned that neither $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ nor $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ could be made to react with the ligand H_2DAPTE under the conditions employed during the study. Reaction of $\text{Cu}(\text{CH}_2\text{COO})_2 \cdot \text{H}_2\text{O}$ with the ligand gave a poor yield of a brown product which could not be correctly identified. The blue copper complex (2) is found to be a dinuclear species and it changes to a deep-violet mononuclear complex when treated with coordinating solvents like DMF or pyridine.

Both the pre-formed complexes of nickel(II) and iron(III), namely $[\text{Ni}(\text{H}_2\text{DAPTE})\text{Cl}_2]$ and $[\text{Fe}(\text{H}_2\text{DAPTE})\text{Cl}_2]\text{Cl}$, failed to react with acetone. But, the *in situ* reactions of the metal salts, ligand and acetone formed the macrocyclic derivatives $[\text{Ni}(\text{TDDH})\text{Cl}_2]$ (7) and $[\text{Fe}(\text{TDDH})\text{Cl}_2]\text{Cl}$ (8) respectively. Varying the proportions of the metal salts and the ligand during the preparation did not have any effect, the same products were always obtained.

The analytical data for the ligand and its complexes are given in table 1. The electrical conductivity, magnetic moment values and electronic spectral data of the complexes are given in table 2. These values support the formulations proposed for the complexes.

Table 1. Analytical data^a (%) for the ligand and its complexes.

Compound	C	H	N	M	Cl
H ₂ DAPTE	60.84 (60.87)	5.76 (5.79)	10.12 (10.14)	—	—
[Co(H ₂ DAPTE)Cl ₂]·H ₂ O (1)	39.59 (39.63)	4.21 (4.24)	6.57 (6.60)	13.78 (13.89)	16.70 (16.75)
[Cu ₂ (H ₂ DAPTE) ₂ Cl ₃]Cl (2)	40.79 (40.92)	3.85 (3.90)	6.81 (6.82)	15.39 (15.46)	17.22 (17.30)
[Pd ₂ (H ₂ DAPTE)Cl ₄] (3)	26.67 (26.63)	2.53 (2.54)	4.48 (4.44)	33.71 (33.73)	22.58 (22.51)
[Co(H ₂ DAPTE)Cl ₂]Cl·H ₂ O (4)	32.70 (30.72)	4.66 (4.67)	5.47 (5.45)	11.43 (11.47)	20.67 (20.74)
[Mn(DAPTE)acac]·H ₂ O (5)	51.08 (51.12)	4.68 (4.70)	6.26 (6.27)	12.26 (12.33)	— —
[Fe ₂ (DAPTE) ₂ (H ₂ O) ₂](ClO ₄) ₂ ·2H ₂ O (6)	36.12 (36.09)	3.85 (3.87)	5.98 (6.01)	12.10 (12.03)	— —
[Ni(TDDH)Cl ₂] (7)	49.73 (49.41)	4.91 (4.94)	5.77 (5.76)	12.11 (12.09)	14.47 (14.62)
[Fe(TDDH)Cl ₂]Cl (8)	46.36 (46.29)	4.58 (4.63)	5.38 (5.40)	10.74 (10.80)	20.57 (20.54)

^aNumbers in parentheses are calculated values.

Molecular weight determinations of the complexes (2) and (3) support their dinuclear nature. The magnetic moment of 3.27 BM for [Fe(TDDH)Cl₂]Cl (8), suggests a $S = 1/2 \rightleftharpoons S = 3/2$ spin equilibrium (Dose *et al* 1976; Mary Elizabeth and Zacharias 1987).

3.2 Infrared spectra

Selected IR frequencies are given in table 3. In uncomplexed H₂DAPTE, $\nu(\text{NH}_2)$ appears at 3300 and 3360 cm^{-1} and $\delta(\text{NH}_2)$ at 1620 cm^{-1} . The $-\text{S}-\text{CH}_2$ stretching modes of the ligand occur at 670 and 700 cm^{-1} . $\nu_{\text{as}}(\text{NH})$ in the metal complexes appears in the 2820–3350 cm^{-1} region and $\nu_{\text{s}}(\text{NH})$ at the 2600–3280 cm^{-1} region, showing bonding of the amine groups to the metal ions. Only one band in this region due to $\nu(\text{NH})$ appears in the cases of [Fe₂(DAPTE)₂(H₂O)](ClO₄)₂·2H₂O (6) and [Mn(DAPTE)acac] (5), showing that deprotonation from the amine functions has occurred in these particular complexes. Bands observed in the lower region (543–330 cm^{-1}) for the complexes (1–3) and (4), (7) and (8) are due to $\nu(\text{M}-\text{Cl}) + \nu(\text{M}-\text{S})$ modes (Nakamoto 1978). The $\nu(\text{S}-\text{CH}_2)$ in the complexes are also shifted suggesting the presence of M–S linkages.

The perchlorate ion is known to change its symmetry from T_d to C_{3v} (unidentate) or C_{2v} (bidentate) and the ν_3 band (at 1100 cm^{-1}) is split into two or more components (Rosenthal 1973; Nakamoto 1978). The presence of three bands in the iron(III) complex (6) can be explained by the fact that the two water molecules are coordinated and that the infrared effects are caused by hydrogen bonding which may place the different O atoms in different environments and induce C_{2v} or C_{3v} symmetry for

Table 2. Molar conductivity (Λ_M), magnetic moment and electronic spectral data for the complexes.

Compound	Λ_M (ohm ⁻¹ cm ² mol ⁻¹)	Room temperature magnetic moment		λ_{max} (cm ⁻¹)
		(B.M.)	(B.M.)	
[Co(H ₂ DAPTE)Cl ₂]·H ₂ O (1)	37.04 ^a	4.34	16129, 19047, 20000, 21978	
[Cu ₂ (H ₂ DAPTE) ₂ Cl ₃]Cl (2)	71.59 ^a	1.16	16393, 28090	
[Pd ₂ (H ₂ DAPTE)Cl ₄] (3)	40.11 ^a	Diamagnetic	25329, 32258, 40000	
[Co(H ₂ DAPTE)Cl ₂]Cl·H ₂ O (4)	75.94 ^b	Diamagnetic	15151, 16949, 20408, 32786, 37735	
[Mn(DAPTE)acac]·H ₂ O (5)	3.77 ^b	5.49	162620, 28985 (sh)	
[Fe ₂ (DAPTE) ₂ (H ₂ O) ₂](ClO ₄) ₂ ·2H ₂ O (6)	34.44 ^a	5.1	20489 (sh)	
[Ni(TDDH)Cl ₂] (7)	20.88 ^c	3.04	10458, 16951, 23645	
[Fe(TDDH)Cl ₂]Cl (8)	58.36 ^a	3.27	17094(sh), 28169(sh), 33444(sh), 43103	

Measured in: ^aDMSO; ^bDMF; ^cCH₃NO₂.

Table 3. Selected infrared frequencies of the complexes (cm⁻¹).

Compound	ν_{as} (NH)	ν_s (NH)	δ (NH ₂)	ν (C=N)	ν (-S-CH ₂)	ν (M-X) + ν (M-S)
H ₂ DAPTE	3360	3300	1620	—	700, 670	—
[Co(H ₂ DAPTE)Cl ₂]·H ₂ O (1)	3350	3280	1615	—	700, 665	—
[Cu ₂ (H ₂ DAPTE) ₂ Cl ₃]Cl (2)	Not clear	Not clear	1600	—	Not clear	Not clear
[Pd ₂ (H ₂ DAPTE)Cl ₄] (3)	3140	3100	1600	—	675, 615	330-255
[Co(H ₂ DAPTE)Cl ₂]Cl·H ₂ O (4)	2820	2600	1605	—	705, 680	470-330
[Mn(DAPTE)acac]·H ₂ O (5)	3350	—	1600	—	665	—
[Fe ₂ (DAPTE) ₂ (H ₂ O) ₂](ClO ₄) ₂ ·2H ₂ O (6)	—	2880	1600	—	665, 640	460-330
[Ni(TDDH)Cl ₂] (7)	—	3280	—	1600	690, 655	545-330
[Fe(TDDH)Cl ₂]Cl (8)	—	3100	—	1600	705, 660	545-385

perchlorate ions. The IR spectral data also support the formulation of nickel(II) complexes $[\text{Ni}(\text{H}_2\text{DAPTE})\text{Cl}_2]$ (Cannon *et al* 1967) and $[\text{Ni}(\text{TDDH})\text{Cl}_2]$ (7). In the latter case, no $\nu(\text{NH}_2)$ bands are observed but a sharp peak appears at 3280 cm^{-1} which is due to $\nu(\text{NH})$. No band was observed at 1600 cm^{-1} for $[\text{Ni}(\text{H}_2\text{DAPTE})\text{Cl}_2]$, but the band at 1600 cm^{-1} for (7) can be tentatively assigned to $\nu(\text{C}=\text{N})$. For $[\text{Fe}(\text{TDDH})\cdot\text{Cl}_2]\text{Cl}$ (8) also, sharp bands at 3100 cm^{-1} (due to $\nu(\text{NH})$) and 1600 cm^{-1} ($\nu(\text{C}=\text{N})$) are observed.

3.3 Electronic spectra

The electronic spectral data of the complexes are summarised in table 2. The bands observed for complexes (1), (4), (5) and (7) suggest their octahedral geometry (Lever 1968; Hathaway and Dilling 1970). A band at $23,529\text{ cm}^{-1}$ (in dichloromethane) for the palladium(II) complex has been assigned to ${}^1A_{1g} \rightarrow {}^1A_{2g}(d_{xy} \rightarrow d_{x^2-y^2})$ in square-planar geometry (Ito *et al* 1967; Day *et al* 1968).

In the Cu(II) complex (2), a band is observed at $28,090\text{ cm}^{-1}$ and a high intensity ($\epsilon = 4093$) band at 16393 cm^{-1} (figure 2). The nature of the spectrum is comparable to those found in 'blue' or type I copper proteins. Type I copper occurs in blue electron-carrying proteins such as stellacyanin, plastocyanin and azurin where it is the only type of copper present. It also occurs, accompanied with types II and III, in blue oxidases, laccase, ceruloplasmin and ascorbate oxidase. By itself, blue copper is characterised by an exceedingly intense electronic absorption at around 600 nm ($16,666\text{ cm}^{-1}$; $\epsilon = 5000$) (Amundsen *et al* 1977). The suggestion that the active sites in type I or blue copper proteins contain at least one sulphur ligand (McLendon and Martell 1977; Hill and Smith 1978) was followed by the determination of the X-ray crystal structures of plastocyanin (Coleman *et al* 1978) and azurin (Adam *et al* 1978) which showed that the copper ion is coordinated both to cysteine mercaptide sulphur and to methionine thioether sulphur, as well as to two histidine imidazole donors. The band near $30,000\text{ cm}^{-1}$ is the blue band and is ascribed to $d_{x^2-y^2} \rightarrow \text{S.C.T.}$

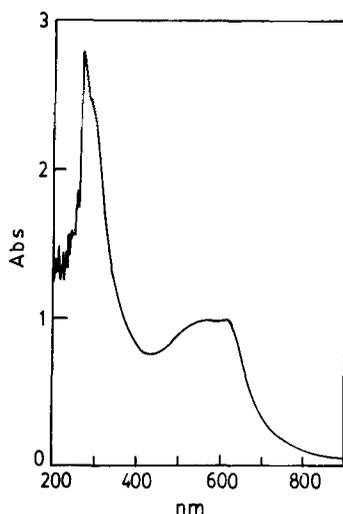


Figure 2. Electronic spectrum of $[\text{Cu}_2(\text{H}_2\text{DAPTE})_2\text{Cl}_3]\text{Cl}$.

excitation and the band at about $17,000\text{ cm}^{-1}$ is assigned to $d-d$ transitions essentially localised at the Cu(II) ion. The $d-d$ bands in these sulphur containing complexes, however, are unusually intense and it seems highly probable that this enhancement arises through borrowing from the higher energy bands, principally the blue band. The blue band arises due to $R_2S(\sigma) \rightarrow d_{x^2-y^2}$ transition. The intensities of such transitions are related to the degree of overlap between the appropriate ligand and metal orbitals. The high intensity band for (2) is due to $d-d$ transition. The other higher energy band is assigned to $R_2S(\sigma) \rightarrow \text{Cu(II) C.T.}$ transition. Therefore, a dinuclear structure is proposed for the complex, similar to that of the copper(II) complex with 1,8-diamino-3,6-dithiaoctane (Amundsen *et al* 1977), which is trigonal bipyramidal bridged through a chloride ion. This may suggest that the present ligand cannot adopt a square-planar arrangement about copper(II) and is stabilised into five-coordinate geometry. No prominent bands have been observed for the iron(III) complex (6). A slight shoulder at $20,489\text{ cm}^{-1}$ may be due to ${}^6A_1(G) \rightarrow {}^4E, {}^4A_1(G)$ transition. The room temperature magnetic moment of 3.27 BM for $[\text{Fe}(\text{TDDH})\text{Cl}_2]\text{Cl}$ (8) suggests that the complex is in spin equilibrium $S = 1/2 \rightleftharpoons S = 3/2$. For such equilibrium, the broad band at $10,000\text{ cm}^{-1}$ can be of ${}^4E \rightarrow {}^6A$ origin (Reiff *et al* 1968) and the $20,000\text{ cm}^{-1}$ shoulder due to ${}^2T_2, {}^2A \rightarrow {}^2T_1$ transition (Ewald *et al* 1969; Butcher *et al* 1976). The transition at $10,000\text{ cm}^{-1}$ is not observed as it is beyond the range of the instrument used. A shoulder at $17,094\text{ cm}^{-1}$ is assigned to ${}^2A, {}^2T_2 \rightarrow {}^2T_1$ transition in the equilibrium system. Other higher energy bands are of C.T. origin.

3.4 Mössbauer spectra

For a system with equilibrium, two types of Mössbauer spectral pattern can arise, depending on the relaxation time relative to the effective quadrupole period. If the time required for relaxation from one spin state to the other is larger, as compared to the quadrupole period, then a spectrum characteristic of the individual spin states is observed. If the relaxation time is less than the effective quadrupole period, an average spectrum results (Mary Elizabathe and Zacharias 1987).

The spectrum of the complex (8) shows a quadrupole splitting value of 0.47 mm/s and an isomer shift value of 0.32 mm/s . The very low quadrupole splitting value of the spectrum suggests that an average spectrum has resulted and the value is comparable to such spin-equilibrium iron(III) complexes (Mary Elizabathe and Zacharias 1987). Room temperature ($S = \frac{5}{2}$) spectra for a series of iron(III) complexes (Kunze *et al* 1977) appear to be the best fits as singlets with positive isomer shifts. As the temperature is lowered, the singlets observed at room temperature for the fully high-spin complexes tend to broaden and remain as singlets or resolve into clearly defined quadrupole-split doublets with ΔE values ranging from $0.19-0.35\text{ mm/s}$. The splitting occurs for intermediate-spin complexes with an increase in low-spin population. This is expected for an increased contribution of the spectrum by the $S = \frac{1}{2}$ state. The other compounds have $S = \frac{5}{2}$ state at low temperatures. Other known cases of intermediate spin with ΔE values of less than 1 mm/s have been reported (Bancroft and Platt 1972; Mitra 1982). Complex (8) has intermediate spin at room temperature and the lower-quadrupole splitting value is contributed by the low-spin state. At lower temperatures the splitting value may increase but, due to lack of facilities, low-temperature spectra could not be recorded by us.

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