

TABLE I
Band head data of NiBr molecule in the region $\lambda\lambda$ 3650–3900 Å

Intensity	Wave-number in vacuum ν cm^{-1}	Assignment ν', ν''	$\nu_{\text{obs}} - \nu_{\text{cal}}$ cm^{-1}	Observed isotopic shift $\nu^{79} - \nu^{81}$ cm^{-1}	Calculated isotope shift $\nu^{79} - \nu^{81}$ cm^{-1}
2	27483.3	2, 0	+0.1	+2.4	+2.3
6	27233.6	1, 0	+0.2	+2.3	+1.1
4	27161.6	2, 1	-0.5	+2.2	+0.9
8	26960.6	0, 0	0.0	0.5	0.1
2	26901.3	1, 1	-0.5	-0.5	-0.4
2	26841.8	2, 2	+0.6	-0.8	-0.7
3	26771.7	3, 3	-0.2	-0.4	-0.9
3	26681.5	4, 4	-0.3	-0.8	-1.1
10	26639.5	0, 1	+0.5	-0.7	-1.7
3	26570.6	1, 2	-0.2	-1.4	-2.0
2	26523.3	2, 3	-0.6	-1.2	-2.4
2	26464.2	3, 4	+0.5	-2.1	-2.6
5	26319.2	0, 2	0.0	-2.2	-3.2
3	26264.0	1, 3	0.0	-4.0	-3.6
2	26207.3	2, 4	-0.3	-3.3	-3.9
3	26000.7	0, 3	-0.5	-3.7	-4.7
3	25911.8	1, 4	+0.4	-4.7	-5.3

Spectrum of NiBr molecule was excited in a high frequency discharge using pure anhydrous sample of NiBr₂. Spectrum in the region $\lambda\lambda$ 3500–5000 Å was recorded in the second order of a 2-meter plane grating spectrograph at a dispersion of 3.59 Å/mm using ORWO WU-3 plates. Measurements of band heads were made against iron-arc standards on Abbe comparator.

The spectrogram (Fig. 1) shows the new red degraded bands in the region $\lambda\lambda$ 3550–3900 Å which get excited along with all bands reported by earlier

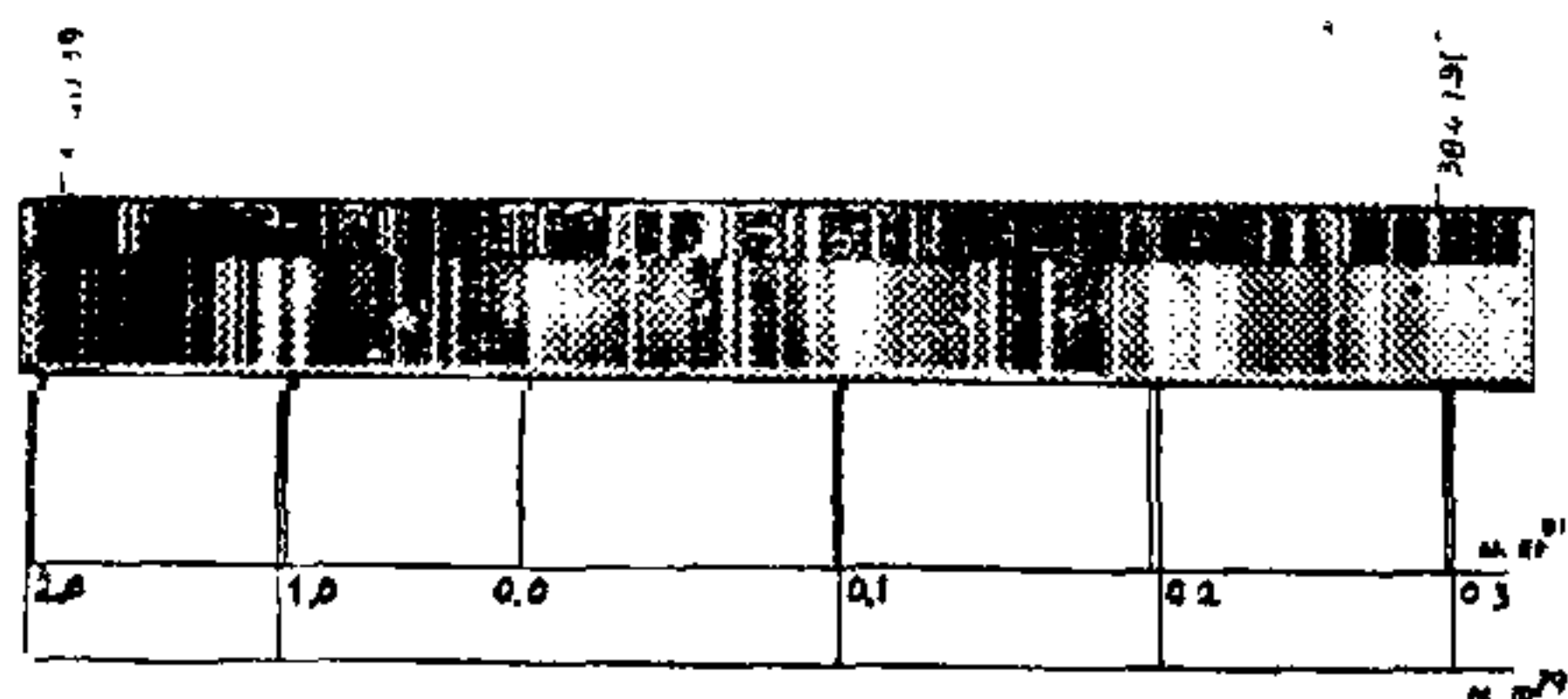


FIG. 1. Grating spectrogram of NiBr bands in the region $\lambda\lambda$ 3550–3900 Å at a dispersion of 3.59 Å/mm.

workers. These bands could not be fitted into any of the vibrational schemes, known so far for NiBr molecule. From the observed regularity of intervals and intensity, the band at 26960.6 cm^{-1} was taken as the (0,0) band and the vibrational analysis was carried out in the usual way. All the observed bands fit into the vibrational equation given below :

$$\begin{aligned} \nu_{\text{head}} = & 26989.7 + 265.7(\nu' + 1/2) \\ & - 1.48(\nu'' + 1/2)^2 \\ & - 323.4(\nu'' + 1/2) \\ & + 0.90(\nu'' + 1/2)^2. \end{aligned}$$

The lower state frequency of 323.4 cm^{-1} obtained in the present work is in agreement with the lower state frequency of β and γ systems of NiBr molecule as reported by Reddy and Rao. The vibrational analysis of the bands is supported by the isotopic shift due to Br⁷⁹ and Br⁸¹. Table I, including the band head data of the bands and isotopic shifts due to Br⁷⁹ and Br⁸¹ reported here, shows close agreement between the observed and calculated values.

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1. Mesnage, P., *Ann. Physique, Fr.*, 1939, 12, 5.
2. Krishnamurty, V. G., *Indian J. of Physics*, 1952, 26, 429.
3. Reddy, S. P. and Rao, P. T., *Proc. Phys. Soc. G.B.*, 1960, 75, 275.
4. Bulewicz, E. M., Philips, L. F. and Suden, T. M., *Trans. Faraday Soc. G.B.*, 1961, 57, 921.
5. Sundarachary, N., *Proc. Nat. Acad. Sci. India, A*, 1962, 32, 311.

INFORMATION ON THE INTERNAL FIELDS THROUGH BETA-GAMMA DIRECTIONAL CORRELATION IN Ho-166

THE ground state decay of ^{166}Ho isotope ($T_{1/2} = 27$ hr) is very well established¹. The 81 keV first excited state in the daughter ^{166}Er nucleus is fed by the beta group with an end-point energy of 1776 keV and has a life-time of 1.83×10^{-12} sec². Considerable attenuation in the angular correlation of the cascade radiations involving the 81 keV level as the intermediate state could therefore be expected and was earlier observed by several investigators³⁻⁶. The cause of such an attenuation is the interaction between the nucleus in this state and the hyperfine field distributions existing within the source material at the site of the nucleus. A careful measurement of the attenuation factors G_2 and G_4 yield information about the internal fields. Bodenshteyn *et al.*⁴, measured the 1380 keV gamma—81 keV gamma angular correlation and obtained information about the internal fields in the HOCl_3 source material. They concluded that the attenuation of the angular correlation in the case of HO-166 is caused by the pure magnetic dipole type of interaction. Later Mellema *et al.*⁶ pointed out that the attenuation factor G_2 obtained from the γ - γ angular correlation measurements in Er-166 is not accurate because of the interference from the P_4 ($\cos \theta$) term as also because of the very weak gamma feeding the 81 keV level. They performed 1776 keV β -81 keV γ angular correlation measurement in Ho-166 using an anthracene crystal for beta detection and concluded that a considerable contribution seemed to appear from the electric quadrupole type of interaction to the otherwise pure magnetic dipole interaction. Also, the G_2 obtained from the β - γ angular correlation measurements would be more accurate because, (1) the P_4 term is absent for the present first-forbidden β transition and (2) because of the large intensity of the beta compared to the 1380 keV gamma feeding the 81 keV level in ^{166}Er . In the present investigation, an attempt is made to re-measure the β - γ angular correlation using a well type NE-102 plastic scintillator possessing superior characteristics over an anthracene crystal in the detection of β -particles. Also, a quantitative information about the internal hyperfine fields is aimed at in the present work.

The set-up used for the present measurements is a conventional fast-slow scintillation assembly. A $1\frac{1}{2}'' \times 1''$ NaI(Tl) crystal enabled the gamma detection. The 27 hr. ^{166}Ho radioactive isotope was obtained from the Isotope Division of Bhabha Atomic Research Centre, Bombay, in the form of HOCl_3 dissolved in HCl. The liquid sources are prepared by sandwiching a drop of HOCl_3 solution between two mylar foils of 0.6 mg/cm^2 thickness, thus forming a well defined circular film-source for the present investigations.

Beta-gamma differential correlation experiments — performed at eight beta energies in the energy range 580–1776 keV. The details of the experimental procedure, various corrections effected were given elsewhere⁷. Correction for finite thickness of the source was done basing on the nomograms of Gimmi *et al.*⁸. The final results of $\epsilon(W)$ and

$$G_2(W) \left(= \frac{\epsilon(W)}{\epsilon_{th}(W)} \right)$$

where

$$\epsilon(W)_{th} = \frac{1}{2} \frac{\lambda_1 p^2}{q^2 + \lambda_1 p^2},$$

λ_1 is the Coulomb correction factor and p and q are the electron and neutrino momenta respectively are shown in Fig. 1. The integral attenuation factor $\bar{G}_2(W)$ is obtained by averaging over all the G_2 values in the entire energy range.

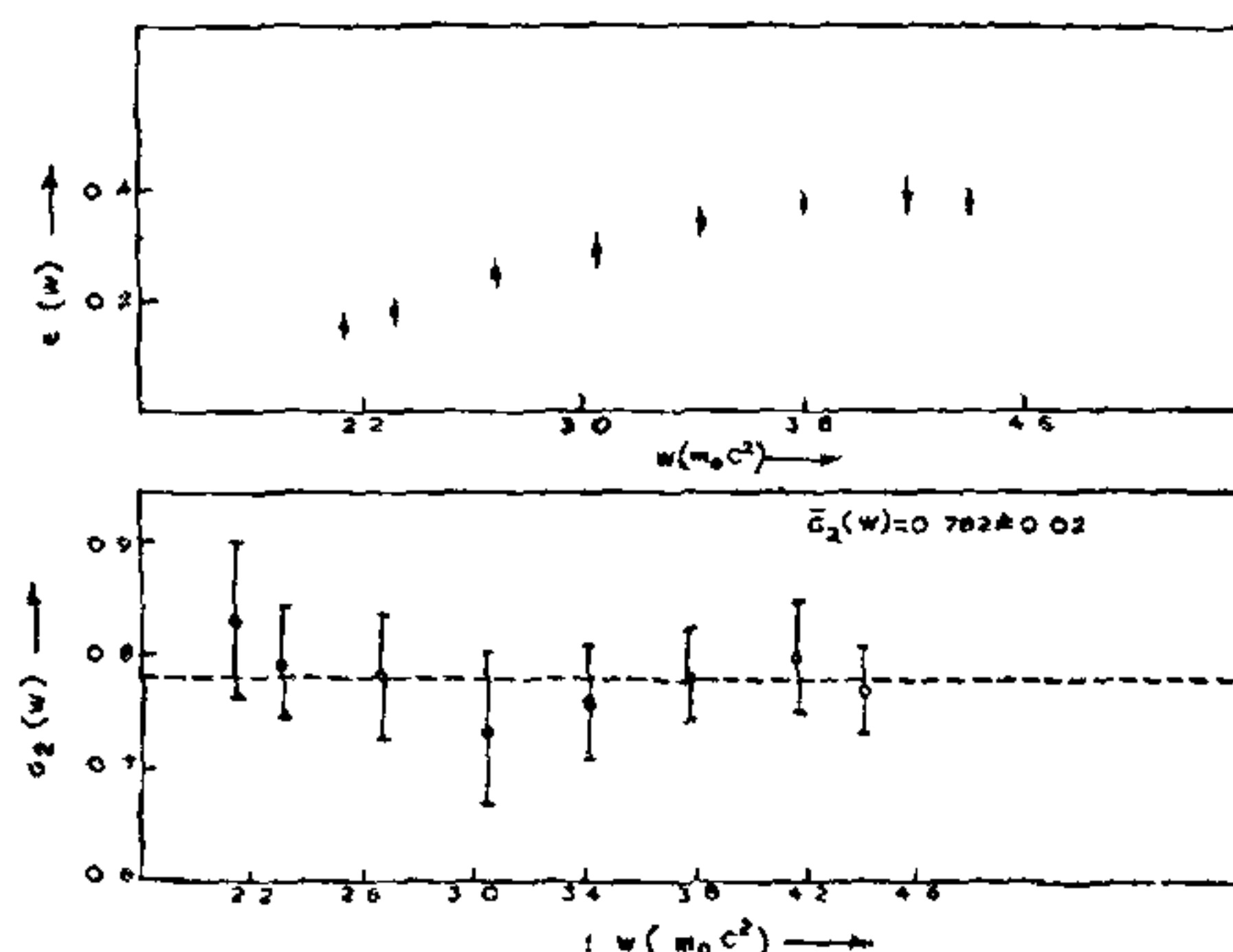


FIG. 1. Energy dependence of the β - γ correlation coefficient $\epsilon(W)$ and the attenuation factor $G_2(W)$ measured in liquid HOCl_3 source.

If we assume a time dependent interaction, the attenuation factor follows the exponential law $e^{-\lambda_k t}$ for randomly fluctuating electric and magnetic fields. The integral attenuation factors \bar{G}_k are related to λ_k through

$$\bar{G}_k = \frac{1}{1 + \lambda_k \tau} \quad (1)$$

where τ is the life time of the intermediate state.

Hence

$$\frac{\lambda_4}{\lambda_2} = \frac{(1 - G_4) G_2}{(1 - G_2) G_4} \quad (2)$$

Using the present value of G_2 (0.782 ± 0.02) and the more recent value of Forker *et al.* (referred in ref. 6) for G_4 0.546 ± 0.009 as obtained from their time differential γ - γ angular correlation measurements, we get

$$\frac{\lambda_4}{\lambda_2} = 2.987 \pm 0.131$$

Theoretical predictions due to Abragam and Pound¹⁰ for the present case involving 0-2-0 spin sequence, are as follows:

$$\frac{\lambda_4}{\lambda_2} = 3.3 \text{ for pure magnetic dipole interaction}$$

$$\frac{\lambda_4}{\lambda_2} = 0.59 \text{ for pure electric quadrupole interaction.}$$

A comparison of our present value of (λ_4/λ_2) with the above theoretical predictions suggests a contribution of about 15% (at its maximum limit) of electric quadrupole type of interaction to the otherwise pure magnetic dipole type.

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1. *Nuclear Data Sheets*, 1975, **14**, 471.
2. Kugel, H. W., Funk, E. G. and Mihelich, J., *Phys. Rev.*, 1968, **168**, 1352.
3. Marklund, I., Van Nooijen and Grabowski, Z., *Nucl. Phys.*, 1960, **15**, 533.
4. Bodenstedt, E., Korner, H. J., Gunther, G. and Radloff, J., *Ibid.*, 1961, **22**, 145.
5. Vervier, J., *J. de Phys.*, 1963, **24**, 763.
6. Mellema, J. and Van der Veen, P. H., *Nucl. Phys.*, 1968, **117A**, 376.
7. (a) Rao, W. V. S., Rao, K. S., Sastry, D. L. and Swami Jnanananda, *Phys. Rev.*, 1964, **SB**, 1193.
(b) Rao, W. V. S., Rao, K. S., Sastry, D. L. and Swami Jnanananda, *Proc. Phys. Soc.*, 1965, **87**, 917.
8. Gimmi, F., Heer, E. and Scherrer, P., *Helv. Phys. Acta*, 1956, **29**, 147.
9. Kotani, T., *Phys. Rev.*, 1959, **113**, 622.
10. Abragam, A. and Pound, R. V., *Ibid.*, 1953, **92**, 943.

Cu(II), Ni(II) AND Fe(II) CHELATES OF 4'-METHYL, 4-HYDROXY, 3-CARBOXY AZOBENZENE

Cu(II), Ni(II) and Fe(II) chelates of 4'-methyl, 4-hydroxy, 3-carboxy azobenzene are prepared and studied. Analytical, magnetic and spectral studies are carried out to determine their stoichiometry and structure. Magnetic moments show the Fe(II) complex to be tetrahedral and other complexes square planar.

Materials and Methods

Metal salts were of BDH (Analar) grade *p*-toluidine and salicylic acid (BDH) were used without further purification.

The ligand was obtained as follows: The *p*-toluidine was diazotized¹ and immediately coupled with salicylic acid in alkaline medium. The solution was acidified with dilute acetic acid and yellowish brown crystals formed were filtered and recrystallized from ethanol (m.p. 148°C). It is soluble in alcohol, benzene, chloroform, carbontetrachloride and pyridine. It is however, slightly soluble in cold water and more so in hot water.

Cu(II) and Ni(II) chelates were prepared by refluxing the solutions of metal chlorides with ligand in alcohol. A little sodium acetate was added. The Fe(II) Chelate was prepared by refluxing the solution of ferrous ammonium sulphate with the ligand in alcohol in an atmosphere of hydrogen. The excess metal or ligand was removed by washing with hot distilled water. The Cu(II) and Ni(II) chelates recrystallized from chloroform and dried at 110°C. The ferrous complex tends to get oxidized in solution but it is quite stable in the solid state. The Cu(II), Ni(II) and Fe(II) chelates are red, yellow and reddish brown respectively. Cu(II) and Ni(II) chelates are insoluble in water but soluble in common organic solvents.

The metals in the chelates were estimated by standard methods². The metal content of the chelates showed the metal : ligand ratio to be 1 : 2. Their molecular weights determined cryoscopically using camphor as a solvent, showed them to be monomeric. The molar conductance was measured in nitrobenzene with a Toshniwal conductivity Bridge. The molar conductances of the chelates were around 5 Ohm cm² mole⁻¹ for 10⁻³ solutions in nitrobenzene, indicating their non-electrolytic nature. The conductivity of ferrous complex could not be determined because of oxidation. The magnetic susceptibilities of the solid complexes were determined at room temperature by the Gouy method. The electronic spectra of the chelates in chloroform were recorded on a Beckman Du Spectrophotometer. I.R. spectra (KBr) of the chelates were recorded in the region 4000-400 cm⁻¹, on a Perkin-Elmer infracord spectrophotometer.

The details of the analysis, molecular weight determination, molar conductance, and magnetic moment are shown in Table 1.

Results and Discussion

I.R. spectra of all the chelates showed that the ligand band 3460 cm⁻¹ indicative of the presence of a free -OH group (Phenolic) is absent in chelates showing that the -OH group takes part in co-ordinating giving

TABLE I

Chelate	% of metal		Mol. wt.		Molar conduc- tance mhos Cm ² mole ⁻¹	μ_{eff} (B.M.)
	found	expected	found	expected		
CuL ₂	11.15	11.08	580	573.54	4	2.1
NiL ₂	10.26	10.34	562	568.71	5.5	Diam.
FeL ₂	9.92	9.94	572	565.85	..	5.28

rise to a C-O-metal bond³. The C=O stretching frequency at 1710 cm⁻¹ in the ligand is lowered to about 1630 cm⁻¹ in the chelates. Thus the carboxyl group co-ordinates through the carbonyl oxygen in the chelates.

The magnetic moment (2.1 B.M.) of the CuL₂ was found to be in slight excess over the "Spin only" value and this may be due to Spin-Orbit coupling⁴. The absorption bands at 645 nm ($\epsilon = 220$) and 590 nm ($\epsilon = 350$) could be due to the transitions $^2A_{1g} \leftarrow ^2B_{1g}$ and $^2E_g \leftarrow ^2B_{1g}$ respectively on the basis of a square planar structure of the copper chelate⁵. The third band at 395 nm ($\epsilon = 10140$) could be an intra-ligand band present in the ligand at 460 nm ($\epsilon = 9640$) possibly $\pi \rightarrow \pi^*$ Transition.

The nickel complex (NiL₂) is diamagnetic, indicating a square planar structure⁶. The absorption bands at 610 nm ($\epsilon = 102$) and 540 nm ($\epsilon = 372$) could arise from the transitions $^1B_{1g} \leftarrow ^1A_{1g}$ and $^1E_g \leftarrow ^1A_{1g}$ respectively⁷. The third band at 380 nm ($\epsilon = 8655$) is the intra ligand band.

The ferrous complex (FeL₂) is paramagnetic with magnetic moment, $\mu_{\text{eff}} = 5.28$ B.M. at 30° C. The slight excess over 'Spin only' value is due to the orbital contribution⁸. This complex is considered to be a tetrahedral structure.

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1. Mohandas, P. N., Sunar, O. P. and Trivedi, C. P., *Indian J. Chem.*, 1973, 11, 73.

2. Vogel (AI), *A Text-book of Qualitative Inorganic Analysis including Elementry Instrumental Analysis*, London, Longmen's Ed., 1964.

3 and 8. Lewis (J) and Wilkins (RG), *Modern Co-ordination Chemistry*, Ed. (1960), 365, 422.

4. Earnshaw (A), *Introduction to Magnetochemistry*, Academic Press, New York, 1968, p. 34.

5 and 6. Figgi (BN), *Introduction to Ligand Fields*, Interscience, 1964, 316, 319.

7. Lever (ABP), *Inorganic Electronic Spectroscopy*, 1968, p. 345.

HYDROGEN PEROXIDE—A NEW SPRAY REAGENT FOR FLAVONES AND QUINONES

A NUMBER of reagents are in use for the detection of flavones and quinones¹⁻⁵. Some of these reagents are specific for skeleton while others are for the presence of hydroxyl groups at certain positions. The present investigation was carried out with a view to finding some new spray reagents for detection of flavones and quinones. The paper chromatographic procedure involving the use of butanol : acetic acid : water. (4 : 1 : 5 v/v) as a solvent system and *hydrogen peroxide* (15%) as spray reagent, have been developed for the detection of 5-hydroxy flavones and α -hydroxy quinones when present in amounts of at least 5 μ g each.

The reagent has been found to be quite efficient in performance in comparison with the known spray reagents¹⁻⁴ (*p*-toluene sulphonic acid, 25% aqueous basic lead acetate, 5% aqueous sodium carbonate and 1% methanolic sodium hydroxide solution). However, the new spray reagent has the added advantage of being specific for the detection of 5-hydroxy flavones and α -hydroxy quinones. The completely methylated flavonoids and anthraquinone do not give colour reaction with the reagent. Interestingly it has been observed that 3',4',5,7 tetra O methyl quercetin does not give colour reaction with the reagent inspite the fact that it contains a hydroxyl group at C₄ adjacent to carbonyl group.