

## LETTERS TO THE EDITOR

### NUCLEAR MAGNETIC RESONANCE OF $\text{Co}^{59}$ IN SOME PENTAMMINE $\text{Co}(\text{III})$ COMPLEXES

CHEMICAL shifts in the nuclear magnetic resonance of  $\text{Co}^{59}$  reported so far by earlier workers<sup>1,3</sup> in several cobaltic complexes appear to have been satisfactorily interpreted on the basis of the ligand field theory. From the n.m.r. data Dharmatti and Kanekar<sup>4</sup> established an order of increasing field strength for a series of ligands which is in general conformity with the spectrochemical series. Their work was restricted to a few representative cobaltic amines. We have now studied several compounds containing pentammine cobaltic ion  $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$  in which the ligand X was varied in order to ascertain its ligand field strength in the pentammine series.

The observed data are given in column 4 of Table I. The shifts have been expressed as

This indicates that the contribution due to the second-order paramagnetism to  $\delta$  decreases in this order.

On the basis of the theory of Griffith and Orgel<sup>5</sup> the ligand field strength should also increase in the same order as given above in this series. The absorption spectra of all these pentammines were also studied in the visible region and from the weak d-d band the energy separation between the ground state  $^1\text{A}_{1g}$  and the excited state of  $^1\text{T}_{1g}$  of the  $d^6$  configuration of cobalt in these complexes was estimated (column 2). The order of the ligand field strengths obtained from these values are in fair agreement with that found from the n.m.r. data although the two results are not identical in all respects.

Using optical data, values have also been calculated for the contribution of second-order paramagnetism to  $\delta$  in all these complexes in the

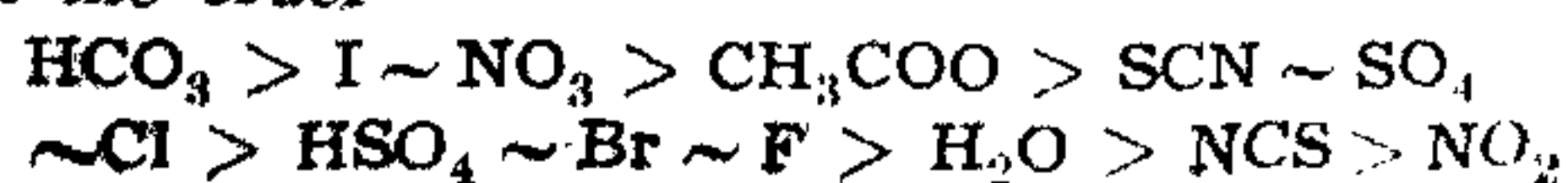
TABLE I

Comparison of the observed chemical shifts with those calculated from ligand field theory

Compound	Energy separation between the ground and the excited state of $d^6$ configuration of cobalt ( $\text{cm.}^{-1}$ )	$\delta\%$	
		Observed	Calculated
1. $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$	21,050	0.75	0.82
2. $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$	20,750	0.749	0.85
3. $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$	20,410	0.831	0.89
4. $[\text{Co}(\text{NH}_3)_5\text{CH}_3\text{COO}](\text{NO}_3)_2$	19,920	0.891	0.96
5. $[\text{Co}(\text{NH}_3)_5\text{NCS}]\text{Cl}_2$	19,840	0.820	0.96
6. $[\text{Co}(\text{NH}_3)_5\text{HCO}_3](\text{NO}_3)_2$	19,680	0.900	0.98
7. $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{Cl}_2$	19,610	0.893	0.99
8. $[\text{Co}(\text{NH}_3)_5\text{SCN}]\text{Cl}_2$	19,610	0.876	0.99
9. $[\text{Co}(\text{NH}_3)_5\text{F}]\text{Cl}_2$	19,610	0.871	0.99
10. $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$	19,050	0.875	1.06
11. $[\text{Co}(\text{NH}_3)_5\text{HSO}_4]\text{Cl}_2$	18,870	0.872	1.09
12. $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	18,870	0.875	1.08
13. $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$	18,350	0.871	1.16
14. $[\text{Co}(\text{NH}_3)_5\text{I}]\text{Cl}_2$	17,240	0.894	1.34

$\delta\%$  defined as  $(H_i - H_r)/H_r \times 100$ , where  $H_i$  is the resonance field for the compound studied and  $H_r$  that of  $\text{K}_3\text{Co}(\text{CN})_6$ , the reference compound. The observed values are negative as the resonance for all these compound occurs at fields much lower than that for the reference.

It is seen from the results that, for the series of ligands X in these pentammines,  $\delta$  decreases in the order



manner indicated by the Griffith-Orgel theory (last column); these values are in fair agreement with the observed data. However, serious discrepancies are observed for the bromo and the iodo complexes; here, the difference between the observed and calculated data is much higher than 20% which is the upper limit of the errors involved in the theoretical calculations. It may be concluded from these results that although the theory of Griffith and Orgel explains the n.m.r. shifts satisfactorily in most

cases it needs refinements. The lack of satisfactory agreement between the theory and experiment for the bromo and iodo complexes may be due to the fact that the model underlying the theory neglects bonding effects; in the halopentammine series where the ionic character of the cobalt halogen-bond decreases from F to I, the discrepancy between the theory and experiment also increases progressively in the series.

Our results also show that the thiocyanato and the isocyanato complexes can be clearly identified with the help of n.m.r. There is a chemical shift of about 5.6 gauss (at 10 K. gauss) between these two isomers. The thiocyanato complex gave two lines; the intensity of one was more than the other. The weaker line was identified to be due to the isocyanato isomer from its position, which corresponded exactly with that of the line observed in a separate experiment for the pure isocyanato complex. It is evident that the thiocyanato complex prepared by conventional method has an impurity of the isocyanato isomer. The absorption maxima corresponding to  $d-d$  transition for the two isomers lie very close to each other ( $510\text{ m}\mu$ ,  $\epsilon_{\text{max.}} = 25.8$  for thiocyanato compound and  $504\text{ m}\mu$ ,  $\epsilon_{\text{max.}} = 51.2$  for the other isomer). It is therefore difficult to distinguish between these isomers from merely their absorption spectra in the visible region.

The authors are thankful to Shri M. A. Pujar, Karnatak University, Dharwar, for preparation of these complexes and Shri V. R. Marathe for running the n.m.r. spectra.

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November 10, 1965.

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## ON LOW-LYING EVEN-PARITY LEVELS OF ${}^2F^{18}$ NUCLEUS

CALCULATIONS<sup>1</sup> for the nuclei with  $A = 18$  have been made on the basis of the intermediate-coupling individual particle model with a modified Gaussian potential and with both Serber and Rosenfeld exchange forces. These nuclei are treated as an even-even core,  $A = 16$  nucleus plus two nucleons in  $1d$  and  $2s$  harmonic oscillator orbitals.

The two-nucleon interaction energy matrices for the ten different states  $(JT) = (10), (30), (40), (50), (11), (21), (31), (41), (01), (20)$ , are constructed and diagonalized following the method of Redlich<sup>2</sup> and Elliot and Flowers<sup>3</sup> with the two-nucleon interaction  $V(r) = (V_0 e^{-r^2/r_0^2}) / (r/r_0)$  where<sup>2</sup>  $V_0 = -70.8$  MeV and  $r_0 = 1.498 \times 10^{-13}$  cm. This potential is intermediary<sup>4</sup> to the usual Yukawa and Gaussian potentials and, in conjunction with the Serber force, explains<sup>5</sup> the ground state binding energies of a large number of nuclei.

TABLE I

Calculated energy level orders of  $F^{18}$  nucleus

State (JT)	Energy (in MeV) with Serber Exchange force	State (JT)	Energy (in MeV) with Rosenfeld Exchange force
$(10)_a$	0	$(10)_a$	0
$(30)_a$	3.093	$(30)_a$	5.433
$(50)_a$	3.662	$(50)_a$	6.800
$(10)_b$	5.158	$(10)_b$	8.445
$(20)_a$	5.537	$(20)_a$	9.113
$(30)_b$	6.635	$(10)_c$	10.50
$(10)_c$	7.396	$(30)_b$	10.89
$(40)_a$	8.705	$(40)_a$	11.88
$(20)_b$	9.549	$(20)_b$	14.24

The suffixes  $a, b$  and  $c$  of the state  $(JT)$  indicate the levels in increasing order,  $a$  being the lowest.

The first few predicted energy levels ( $T = 0$ ) for  $F^{18}$  nucleus with both the Serber and Rosenfeld forces are given in Table I. Here the lowest  $J = 1$  and  $T = 0$  energy is treated as the observed ground state of the  $F^{18}$  nucleus and the remaining levels are calculated relative to this energy. The relative positions of the energy levels with  $T = 1$  with respect to those with  $T = 0$  as well as the level spacings within the  $T = 1$  group are found to be highly sensitive to the assumed exchange character. A study and comparison of these levels with the observed levels (with  $T = 1$ ) in  $O^{18}$  nucleus will be reported later.

A comparison of the predicted energy spacings with those experimentally observed indicates that the predicted energy spacings are large. The estimated energy spacings are enhanced even