

Mossbauer Studies on Some Fe(III) Complexes

C. L. SHARMA,* ASHOK KUMAR SINGH and LAKSHMI DEVI

Chemistry Department, University of Roorkee, Roorkee (India)

Manuscript received 9 November 1976; revised 28 February 1977, accepted 18 March 1977

Mossbauer studies on $Fe(imide)_3$, $[Fe(imide)_3Am_3]$ and $[Fe(imide)_3(en)(H_2O)]$ where imide = phthalimide or succinimide ion, Am = ammonia, methyl amine or ethyl amine, en = ethylenediamine have been carried out at $25 \pm 1^\circ$. The data have been correlated with the stereochemistry and / or magnetic properties of the complexes.

THERE is a pronounced difference in the structure of $FeCl_3 \cdot 6H_2O$ and anhydrous $FeCl_3$ in their crystals. This difference is reflected in the Mossbauer spectra of these two forms^{2,3}. It was considered worthwhile to study the M. B. spectra of a few iron(III) complexes wherein these chloride ions or water molecules are replaced by other large groups which are anionic or neutral in nature. With this in view $Fe(Phthalimide)_3$ and $Fe(succinimide)_3$ have been studied. Phthalimide and succinimide act as an anion after the imino hydrogen has been replaced. Coordination of the carbonyl is not favoured as that would involve the formation of unstable four membered ring. The compounds $[Fe(Phthalimide)_3Am_3]$ and $[Fe(succinimide)_3Am_3]$ where Am = ammonia, methyl amine or ethyl amine were also investigated. In these compounds three water molecules are replaced by three bulky anionic groups and three by amino groups. They are inner complex salts and hence their spectra were compared with $[Fe(terpy)_3Cl_3]^+$.

Experimental

$Fe(Ph)_3$, $[Fe(Ph)_3Am_3]$ where Ph = Phthalimide, and $[Fe(Ph)_3(en)H_2O]$ where en = ethylenediamine were prepared by the method reported earlier^{5,6}. $Fe(succ)_3$, $[Fe(succ)_3Am_3]$ where succ = succinimide and $[Fe(succ)_3(en)H_2O]$ were also similarly prepared. The composition and structure of all the above complexes were checked by chemical analysis, i.r., conductivity and magnetic measurements.

Mossbauer spectra of the complexes were recorded at $25 \pm 1^\circ$ on a Mossbauer spectrometer using a 256-channel analyser and Kankeleit type constant acceleration drive⁷. The source used was ~ 5 m Ci Co^{57} isotope in Palladium matrix. The calibration of the spectrometer was done by the peak positions of standard absorber Sodium Nitroprusside which were prepared by evenly spreading the samples on cello tape.

Chemical shifts δ (mm/sec.) and the quadrupole splittings ΔE (mm/sec.) are given in table 1.

* 134/3 Vikas Nagar, University of Roorkee, Roorkee.

TABLE 1—CHEMICAL SHIFTS (δ) AND QUADRUPOLE SPLITTINGS (ΔE) AT $25^\circ C$ WITH RESPECT TO SODIUM NITROPRUSSIDE ABSORBER.

Substance	δ (mm/sec)	ΔE (mm/sec.)
$FeCl_3$ (ref. 3)	0.80 ($-196^\circ C$)	—
$Fe(phthalimide)_3$	0.58 ± 0.03	—
$Fe(Succinimide)_3$	0.59 ± 0.03	—
$FeCl_3 \cdot 6H_2O$ (ref. 2)	0.65 ($-196^\circ C$)	0.50 ($-196^\circ C$)
$[Fe(terpy)Cl_3]$ (ref. 4)	0.34	0.55
$[Fe(imide)_3Am_3]$	0.58 ± 0.01	0.64 ± 0.03
$[Fe(imide)_3enH_2O]$	0.55 ± 0.03	0.69 ± 0.03

imide = succinimide or phthalimide

Am = ammonia, methyl amine or ethyl amine.

Results and Discussion

$[Fe(imide)_3]$ where imide = phthalimide or succinimide ion. In these complexes, the replacement of chloride ions by imide ions results in a decrease in isomer shift values indicating the greater electron density at the nucleus. No quadrupole splitting is observed because the symmetry of iron in these complexes remains the same as in anhydrous $FeCl_3$. As pointed out earlier, the imide ion does not function as a chelating agent.

In the complexes of the type $[Fe(imide)_3Am_3]$, there is a decrease in isomer shift and increase in quadrupole splitting which again indicate the greater electron density at the nucleus in comparison to $FeCl_3 \cdot 6H_2O$. No appreciable difference in the isomer shift of $Fe(imide)_3$ and $[Fe(imide)_3Am_3]$ indicate that amines are very weakly coordinated to the metal. All the complexes are paramagnetic with a magnetic moment 5.8 B.M., characterised of high spin Fe(III) compounds.

$[Fe(imide)_3(en)(H_2O)]$ complexes show a chemical shift (0.56 mm/sec) characteristic of spin free octahedral Fe(III), and the values are close to that observed

by Maddock et al⁸. Thus it may be concluded that the complexes are octahedral and the water molecule is coordinated to the iron ion.

Acknowledgement

The authors are grateful to Dr. I.P. Saraswat, Head of the Chemistry Department and Sri Ajai Singh for suggestions and providing laboratory facilities.

References

1. F. A. COTTON and C. WILKINSON, *Advanced inorganic chemistry*, II edn. 714, (Inter Science, Publisher Inc. N.Y).
2. J. DONAN, *Notas Fis.*, 1963, 10, 331 cited in Mossbauer effect data index, edited by Arthur H. Muir (Jr), J. KEN and M. C. Helen (I. P. Inc. N.Y.) 1966, 67.
3. DE BENEDETH, S. LANG and G. L. INGALLS, *Phys. Rev. Lett.*, 1961, 6, 60.
4. W. M. REIFF, W. A. BAKER, JR and N. E. FRICKSON, *J. Amer. Chem. Soc.*, 1968, 90, 4794.
5. G. NARAIN, *Z. Anorg. Allegem. Chem.*, 1966, (1 and 2), 343, 12, 109.
6. G. NARAIN, *J. Inorg. Nuclear Chem.*, 1966, 28, 2403.
7. E. KANKLENT, Velocity spectrometer for Mossbauer experiments, *Rev. Sci. Instrn.*, 1964, 35, 194.
8. A. G. MODDOCK, L. O. MEDENOS and G. M. BANCRAFT, *Chem. Commun.*, 1967, 20, 1067.