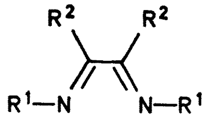
Free-radical Complexes of Closed-shell Metal Ions

By P. CLOPATH and A. v. ZELEWSKY*

(*Institute of Inorganic Chemistry, University of Fribourg,* CH-1700 *Fribourg, Switzerland*)

Summary E.s.r. measurements of 1 : 1 complexes of closed-shell metal ions with the radical anion of glyoxal-bis-*N*-t-butylimine are reported.

WE have begun a systematic study of chelating free radicals and their complexes with closed-shell metal ions.


(I)

A class of radicals suitable for complex formation can be obtained from molecules containing the fragment (I).

We have observed e.s.r. spectra of a series of d^0 and d^{10} metal complexes (1 : 1) with different free-radical ligands of this type, including αα′-bipyridyl and *o*-phenanthroline. Particularly clear results have been obtained from the e.s.r. spectra of 1 : 1 complexes derived from glyoxal-bis-*N*-t-butylimine ($R^1 = Bu^t$, $R^2 = H$).† The parent molecule can be reduced by potassium to the radical anion (L) *e.g.* in dimethoxyethane as solvent. The e.s.r. spectrum of this radical shows a hyperfine structure due to 2 equivalent protons (R^2), 2 equivalent ^{14}N nuclei and 18 equivalent

---

† An e.s.r. spectrum of a molybdenum–carbonyl complex containing this ligand has been observed by F. Gerson and his co-workers (unpublished results).

protons of the 2 t-butyl groups (R^1). The coupling constants for the 3 different sets of nuclei are given in the Table. In dimethoxyethane 1 : 1 metal complexes are obtained by saturating a dilute solution of the free-radical anion with anhydrous metal halides MX_2 or MX_3 (M = Be, Mg, Ca, Zn, Al, Sc, Y; X = Cl, Br, I). The Figure shows the e.s.r. spectrum formed with $MgCl_2$; similar spectra are observed with the other metal halides, but, the small splitting of the t-butyl protons is not resolved in most other cases. The fact that the equivalent sets of nuclei of the ligand remain equivalent upon complex formation reveals the symmetrical structure of the complex. A particularly interesting feature is the occurence of a quartet structure due to one chlorine nucleus. In most of the spectra observed for the bivalent metals one halogen contributes to the hyperfine pattern with the coupling constants increasing strongly in the order Cl < Br < I. Identical high-resolution spectra were obtained from the three calcium halides without halogen hyperfine structure. This indicates that no co-ordination of the halides occurs under the present conditions.

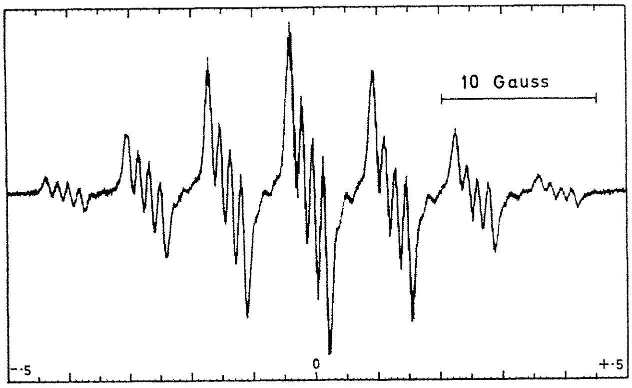


FIGURE. *E.s.r. spectrum of the complex from* $MgCl_2$ *with the radical anion.* $a_H(R^2) = 5{\cdot}30$ G, $a_N = 5{\cdot}30$ G, a_H(t-butyl) = 0·10 G, $a_{Cl} = 0{\cdot}73$ G.

Coupling constants[a]

Species	$a_H(R^2)$	a_N	a_X[c]	a_H (Bu^t)
L	4·3	5·6	—	0·15
MgLCl	5·3	5·3	0·73	0·10
MgLBr	5·4	5·4	4·6	u
CaL(Cl)	5·0	5·5	u	(0·05)[b]
CaL(Br)	5·0	5·5	u	u
CaL(I)	5·0	5·5	u	u
ZnLCl	5·6	5·6	0·58	u
ZnLBr	5·6	5·6	3·4	u
ZnLI	5·6	5·6	4·5	u

[a] All splitting constants are given in Gauss.

[u] Not observed.

[b] Only partially resolved.

[c] X = ^{35}Cl; $^{79,81}Br$ (average); ^{127}I.

Complexes containing metals with magnetic nuclei (^9Be, ^{27}Al, ^{45}Sc, ^{89}Y, and enriched (99·21%) ^{25}Mg) show more complicated e.s.r. spectra owing to hyperfine interaction with the metal nuclear spin.

Radical complexes of the same type were also obtained by direct reaction of magnesium metal with the unreduced ligand in a solution containing magnesium chloride.

These results show the existence of chelate-free radical complexes of closed-shell ions and prove the delocalisation of the unpaired electron over the whole complex species including the halogen ligands.

This work was supported by a grant from the Swiss National Foundation for Scientific Research.

(*Received, October* 23*rd*, 1970; *Com.* 1830.)