Inorganica Chimica Acta, 54 (1981) L35–L37
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

X-Ray Spectroscopic Investigation of Electronic Structure of Lamellar Compounds of Graphite with Co and $CoCl_2$

A. T. SHUVAYEV, A. P. KOSINOV

Institute of Physics, Rostov State University, Rostov, U.S.S.R.

YU. N. NOVIKOV, N. D. LAPKINA and M. E. VOL'PIN

The Institute of Organoelement Compounds, Academy of Sciences of the U.S.S.R., Moscow, U.S.S.R.

Received January 30, 1981

The lamellar compounds of graphite (LCG) with transition metals are known [1–3] to have a structure wherein the atoms of transition metals are disposed between carbon layers and interact with carbon atom nets, the pattern of interaction being dependent on the nature of the metal used. For example, according to X-ray diffraction analysis data and magnetic measurements, a sandwich-type structure is assigned to LCG-Mo [3]. Determining the structure of LCG-Co involved far greater difficulties. On the one hand, the distance between the carbon atom nets of graphite equals 5.8–5.9 Å and can be visualized as the sum of the Van der Waals thickness of the carbon atom net of graphite and the atomic diameter of cobalt, while, on the other hand, the Mössbauer spectroscopy data for LCG-Co^{57} point to the presence of cobalt in these compounds in the form of paramagnetic complexes alongside the superparamagnetic and sometimes also ferromagnetic clusters of cobalt [4].

This paper presents the results of examining by X-ray spectroscopy the electronic structure of LCG-Co and the nature of Co atom interaction with the carbon atom net of graphite. The feasibility of employing this method for determining the pattern of Co interaction with graphite was demonstrated [5–7], and it was shown that the $K\beta_5$ spectra of the atoms of 3d metals in complex compounds reflect the structure of several perturbed levels of ligands and also the 3d levels of metals in case metal–metal bonds are available or the centre of symmetry is absent in the complex. In other words, if Co forms a complex with graphite, in the Co $K\beta_5$ spectrum should appear the graphite bands that interact in a conspicuous manner with the 4p orbitals of Co. The most intense interaction of Co 4p orbitals must involve the π-orbitals of graphite directed into the space between the graphite networks, the Co atoms being disposed in this space analogously to the position of metal atoms in the molecules of ferrocene or dibenzene chromium [5–8]. Moreover, consideration should be given to the fact that transition from LCG-$CoCl_2$ to LCG-Co is to result, in conjunction with the incorporation of Co atoms into the electroconducting system of graphite, in the onset of a red shift of the Co absorption band K edge and in the associated essential dimunution of the intensity of short-wave satellites in the 7712–7720 eV energy range. The intensity of satellites may experience variations also due to alterations in the total spin of the cobalt 3d shell.

Experimental

The secondary Co $K\beta_5$ spectra of the compounds studied were recording using a Type DPC-2 X-ray spectrometer with a spherical quartz crystal (1340) and an X-ray tube (Type БXB-Cu) operated at 30 kV and 80 mA. The time of exposure was 80 hours, the instrumental line broadening being about 0.3 eV for the Co $K_{1,2}$ doublet. To reliably determine the details, $K\beta_5$-spectrum contouring was performed after averaging 4 or 5 high-quality spectrograms.

The LCG-$CoCl_2$ was prepared by the procedure described [9]. The reduction of LCG-$CoCl_2$ with sodium in liquid ammonia, lithium naphthalenide, lithium diphenylide and sodium borohydride was performed according to the procedure reported earlier [2], while the reduction with metallic potassium was carried out as described [10]. The methods of preparing LCG-$CoCl_2$ and LCG–Co and their analyses are listed in Table I.

Results and Discussion

In Fig. 1 are correlated (by means of bringing in coincidence the Fermi energy in energy scale units) The Cl $K\beta$ spectrum of $CoCl_2$ (spectrum 1) [11], Co $K\beta_5$ spectrum of $CoCl_2$ (spectrum 2) and Co $K\beta_5$ spectrum of LCG-$CoCl_2$ (spectrum 3), and also the $K\alpha(\pi)$ spectrum of carbon which presents the structure of the π-band of graphite [12]. As can be seen in Fig. 1, the system of components in the Co $K\beta_5$ spectrum of LCG-$CoCl_2$ provides an adequately distinct presentation of the energy structure of $CoCl_2$, so that the structure of $CoCl_2$ levels experiences no marked changes after $CoCl_2$ intercalation in graphite. It should be emphasized that the Co $K\beta_5$ spectra of LCG-$CoCl_2$ contain no levels corresponding to the energy structure of graphite, this being indicative of the absence of interaction between $CoCl_2$ with graphite networks in the LCG-$CoCl_2$. The principal aspects of the Co $K\beta_5$ spectrum (B, C, and D components) reflect the structure of the

TABLE I. Preparation and Composition of LCG-$CoCl_2$ and LCG-Co.

Sample	LCG* with	Reducing agent	Treatment after reduction	Content of Co, %
a	$CoCl_2$	–	–	18.4
b	Co	Na in liquid NH_3	–	19.1
c	Co	Na in liquid NH_3	washed with EtOH, HCl and H_2O	
d	Co	Na in liquid NH_3	washed with EtOH, HCl and H_2O, and heated in H_2 at 400 °C	22.0
e	Co	lithium naphthalenide	–	19.6
		lithium naphthalenide	washed with EtOh, HCl and H_2O	21.0
g	Co	lithium diphenylide	–	20.0
h	Co	$NaBH_4$	–	22.6
i	Co	potassium at 100 °C	–	19.3

*All the LCG were stage I compounds (the stage denotes the number of carbon atom nets of graphite per layer of intercalated species).

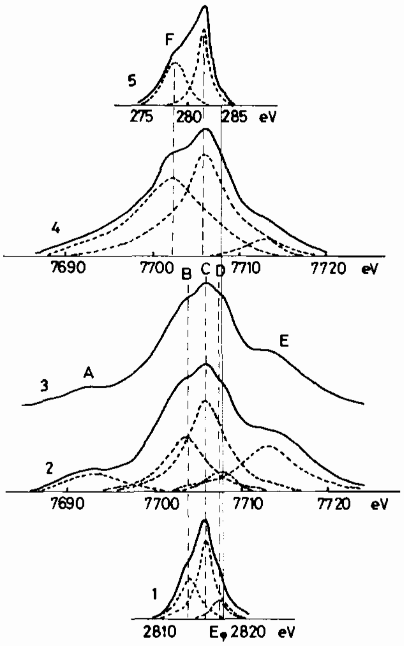

Fig. 1. X-ray spectra of graphite, $CoCl_2$ and lamellar compounds of graphite with $CoCl_2$ and Co: 1 – Cl Kβ spectrum of $COCl_2$; 2 – Co Kβ_5 spectrum of $CoCl_2$; 3 – Co Kβ_5 spectum of LCG-$CoCl_2$; 4 – Co Kβ_5 spectrum of LCG-Co prepared by reducing the specimen *a* in liquid ammonia (specimen *c*): 5 – C K$\alpha_{(\pi)}$ spectrum of graphite. The dashed line indicates the result of resolving the spectra into dispersion components.

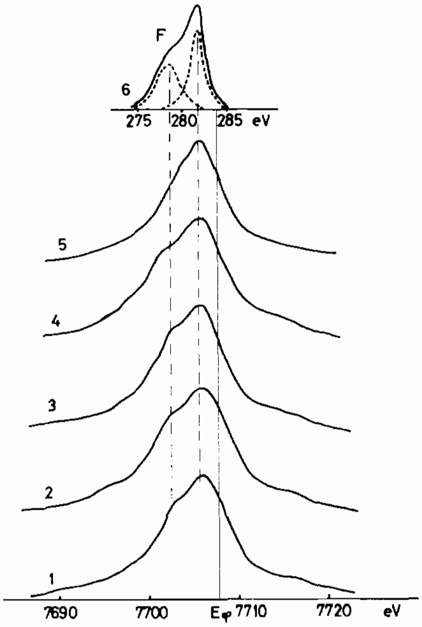

Fig. 2. X-Ray Co Kβ_5 spectra of LCG-Co: 1 – reduction by lithium naphthalenide (specimen *e*); 2 – reduction by lithium naphthalenide (specimen *f*); 3 – reduction by lithium diphenylide (specimen *g*); 4 – reduction by $NaBH_4$ (specimen *h*); 5 – reduction by metallic potassium (specimen *i*); 6 – CK$\alpha_{(\pi)}$ spectrum of graphite.

Cl Kβ spectrum, and this situation is not surprising, inasmuch as the chlorine atoms in the compound in question function as ligands for Co. On the same grounds, in the Co Kβ_5 spectra there manifests itself the 3s level of chlorine (A component), which could not appear in the Cl Kβ_5 spectrum because of selection rules. The presence of a rather intense satellite (E component) is a distinctive characteristic of the Kβ_5 spectrum of $CoCl_2$ and LCG-$CoCl_2$.

LCG-$CoCl_2$ reduction with sodium in liquid ammonia resulted in a sharp change of the spectra (Fig. 1, spectrum 4). In the spectrum, there disappeared the A, B, and D components which correspond to chlorine levels and the intensity of the

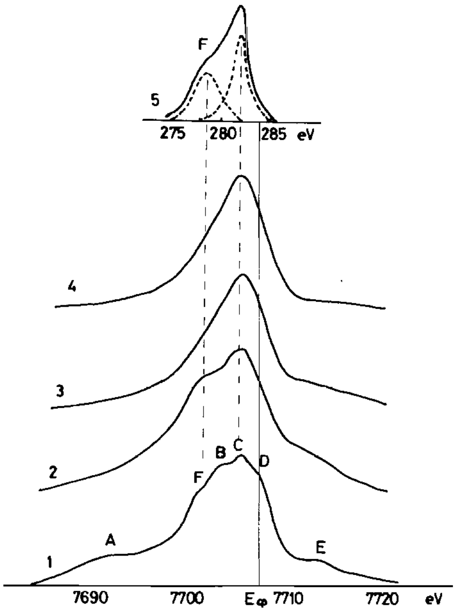

Fig. 3. X-Ray Co Kβ_5 spectra of LCG-Co: 1 – reduction by Na in liquid NH_3 (specimen *b*); 2 – reduction by Na in liquid NH_3 and washing with ethanol, HCl and H_2O (specimen *c*); 3 – reduction by Na in liquid NH_3, washing with ethanol, HCl and H_2O, and heating in H_2 at 400 °C (specimen *d*); 4 – Co Kβ_5 spectrum of metallic Co; 5 – C K$\alpha_{(\pi)}$ spectrum of graphite.

satellite E varied markedly. These alterations point to the reduction of $CoCl_2$ in LCG-$CoCl_2$. It is noteworthy that the F component corresponding to the distinctive features in the π-band of graphite appeared in the spectra and hence the π-levels of graphite are conspicuous in the LOG-Co spectrum (*cf.* spectrum 5 in Fig. 1). Therefore, the Co atoms in LCG-Co do form π-complexes with graphite, the carbon atom network in graphite functioning as π-ligand in these complexes.

Analogous complexes are likewise formed when use is made of lithium naphthalenide, lithium diphenylide or sodium borohydride as reducing agents (spectra 1–4 in Fig. 2). In all instances, the spectra contain no components that correspond to cobalt chloride levels, the intensity of the short wave satellite E drops markedly, and carbon levels manifest themselves. It should be noted that the Co Kβ_5 spectrum of LCG-Co prepared using lithium diphenylide as the reducing agent displays a number of distinctive features, which are likely to accrue from the presence of impurities in the reduction products. A somewhat different result was obtained when LCG-$CoCl_2$ reduction was effected by metallic potassium. Here the Co Kβ_5 spectrum (spectrum 4 in Fig. 2) contains a significantly weaker π-band of graphite and resembles the spectrum of metallic cobalt (spectrum 4 in Fig. 3), this observation being indicative of a substantial degree of cobalt cluster formation.

The influence exerted by the method of LCG-Co treatment on X-ray spectra is illustrated in Fig. 3. The LCG-Co prepared by reduction with sodium in liquid ammonia resists the attack of organic solvents, HCl or water (spectrum 2 in Fig. 3), but decomposes readily when heated in a stream of hydrogen at 400 °C (spectrum 3 in Fig. 3) and yields metallic cobalt clusters, as evidenced by the fact that the shape of the Kβ_5 spectrum of the LCG-Co in this base is similar to that of Kβ_5 of metallic cobalt (spectrum 4 in Fig. 3). The LCG-Co obtained by using other reducing agents undergo decomposition in an analogous manner when heated at 400 °C.

It follows from the foregoing discussion that LCG-$CoCl_2$, under the effect of various reducing agents, yield the LCG-Co in which Co atoms form π-complexes with the aromatic network of graphite. Analogous studies of Fe Kβ_5 spectra of LCG-Fe demonstrated that in this case iron atoms also form π-complexes with the carbon atom net of graphite [13].

References

1 Yu. N. Novikov, M. E. Volpin, Yu. T. Struchkova and V. A. Semion, *Zh. Obshch. Khim.*, *41*, 242 (1971).
2 M. E. Volpin, Yu. N. Novikov, E. D. Lapkina, *et al.*, *J. Am. Chem. Soc.*, *97*, 3366 (1975).
3 *Materials Science and Engineering, 31*, 1–356 (1977).
4 V. E. Prusakov, Yu. N. Novikov, R. A. Stukan, M. E. Volpin and V. I. Goldansky, *Dokl, AN S.S.S.R.*, *207*, 1394 (1972).
5 V. I. Nefedov *et al.*, *Zh Struk. Khim.*, *13*, 637 (1972).
6 A. T. Shuvayev *et al.*, *Izv. AN SSSR, ser. Fiz.*, *40*, 333, 346 (1976).
7 I. A. Zarubin, A. T. Shuvayev, V. V. Tyazhkorob and V. I. Dankshim, *Izv. AN SSSR, ser. Fiz.*, *40*, 340 (1976).
8 V. N. Uvarov, *Thesis*, Rostov University, Rostov-on-Don, 1976.
9 Yu. N. Novikov, N. D. Lapkina, Yu. T. Struchkov and M. E. Volpin, *Zh. Struk. Khim.*, *17*, 756 (1976).
10 Yu. N. Novikov, V. A. Postnikov, A. B. Nefedyev and M. E. Volpin, *Izv. An SSSR, ser. Khim.*, 2381 (1975).
11 V. V. Nemoshkalenk *et al.*, 'Electronic Structure of Chlorides of Some 30 Metals', Preprint, IMF, Kiev, 1975.
12 Ch. Beyrenther and C. Wiech, *Phys. Fennice*, *9*, 176 (1974).
13 A. T. Shuvayev, B. A. Kondakov *et al.*, *Zh. Struk. Khim.*, *20*, 4, 736 (1980).