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Lamellar Compounds of Graphite with Transition Metals. Graphite as a Ligand

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Abstract: Lamellar compounds of chromium, molybdenum, tungsten, iron, cobalt, nickel, manganese and copper with graphite were obtained and their structure, magnetic properties, and Mössbauer spectra were studied. Molybdenum was shown to form sandwich type π-complexes with graphite, similar to dibenzenemolybdenum, in which graphite acts as an aromatic π-ligand. Arguments were presented suggesting that in graphite compounds with iron, cobalt, and nickel some part of the metal forms weak complexes with graphite.

Carbon atoms in graphite are well known to be arranged in layers, and each layer is a regular hexagonal net of carbon atoms (Figure 1). The C–C distances in a layer are 1.41 Å which is close to the bond length in aromatic hydrocarbons. The interlayer spacing is equal to 3.35 Å which corresponds to van der Waals interaction. Such difference in layer and interlayer bond types makes possible formation of lamellar compounds of graphite (LCG)—the products of insertion of different substances into the interlayer space. At present LCG with alkali and alkali earth metals, acids, halogens, and metal chlorides are described.[1-9] The number of carbon layers of graphite per each layer of inserted substance in an LCG is usually called the stage of LCG (Figure 2). The bonding between an inserted substance and a carbon net of graphite depends on the compound inserted and is known to be of either charge transfer or van der Waals type.

However, if a carbon net of graphite is considered as an infinite aromatic molecule, the formation of another type of LCG, namely, complexes of graphite with transition metals, could be expected. In these complexes the carbon net of graphite should act as a polynuclear aromatic ligand. In accordance with Sidgwick's rule, zero-valent metals of group VI (Cr, Mo, W) form stable bis(arene) complexes. Thus, LCG with these metals can be expected to have a bis(arene) structure. Similar bisarenic complexes could also be expected for Mn(I), Fe(II), Co(III), etc. π-Complexes of allylic and olefinic types should be possible in the case of zero-valent Fe, Co, Ni, Mn, and Cu. Formation of such π-complexes would require localization of a certain number of bonds in the conjugated graphite system at the expense of some resonance energy. However, this loss might be compensated by the energy of complex formation. Actually examples are well known in which a metal atom breaks the conjugation system of benzene producing allylic complexes.[10] However, zero-valent metal LCG could *a priori* have another structure with only weak van der Waals interaction between metal atoms and graphite layers or that of the charge transfer complex type.

The present paper deals with the synthesis of LCG with transition metals iron, cobalt, nickel, chromium, molybdenum, tungsten, manganese, and copper and with a study of their structure by X-rays, Mössbauer spectroscopy, and magnetic measurements.

Transition metal LCG were prepared by reduction of the metal chloride LCG ($FeCl_3$, $FeCl_2$, $CoCl_2$, $NiCl_2$, $MnCl_2$, $CuCl_2$, $MoCl_5$, WCl_6, $CrCl_3$). Reduction by means of different reducing agents, hydrogen, sodium borohydride, lithium aluminum hydride, sodium in liquid ammonia, and aromatic anion-radicals (Li, Na, and K naphthalenide and diphenylide and sodium benzophenone ketyl), has been studied.

Reduction of the $FeCl_3$ LCG by sodium in liquid ammonia has been previously described by Klotz and Schneider;[11] reduction of $FeCl_3$ to Fe(0) is reported to take place. Later Knappwost and Metz[12-14] confirmed this result and studied magnetic properties of Fe LCG. According to their data iron is not chemically bonded to carbon nets of graphite in the compounds obtained.

Experiments and Results

Starting Compounds. The starting compounds were $MoCl_5$, $FeCl_2$, $FeCl_3$, $CoCl_2$, $NiCl_2$, $MnCl_2$, WCl_6, $CrCl_3$, and $CuCl_2$ LCG of a definite stage and good regularity.

Table I. The Identity Periods (I_c) and Thicknesses of the Filled Layers (I_c') of Metal Chloride LCG and Metal LCG

Metal chloride LCG	$C/MCl_n{}^a$	Stage	I_c, Å	I_c', Å	Metal LCG	Stage	I_c, Å	I_c', Å	ΔI_c, Å^b
$FeCl_3$	9	I	9.42	9.42	Fe	I	5.9	5.9	3.5
$FeCl_3$	18	II	12.66	9.31	Fe	II	9.5	6.15	3.2
$CoCl_2$	7	I	9.45	9.45	Co	I	5.8	5.8	3.6
$CoCl_2$	13	II	12.74	9.39	Co	II	9.3	5.95	3.4
$MnCl_2$	9	I	9.50	9.50	Mn	I	5.8	5.8	3.7
$NiCl_2$	6	II	12.70	9.35	Ni	II	9.3	5.95	3.4
$CuCl_2$	6	I	9.42	9.42	Cu	I	5.8	5.8	3.7
$CuCl_2$	12	II	12.75	9.40	Cu	II	9.3	5.95	3.4
$MoCl_5$	21	II	12.54	9.19	Mo	II	7.3	3.95	5.2
$MoCl_5$	34	III	16.02	9.32	Mo	III	10.4	3.7	5.6
$MoCl_5$	42	IV	19.37	9.32	Mo	IV	13.7	3.65	5.7

[a] Amount of carbon atom per 1 molecule of metal chloride. [b] $\Delta I_c = I_c(MCl_n\ LCG) - I_c(M\ LCG)$.

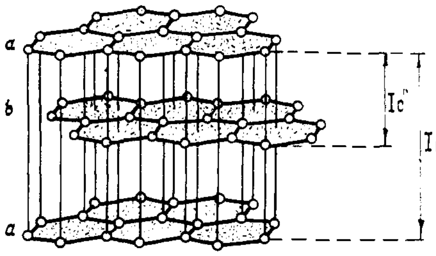

Figure 1. Structure of graphite.

Compounds with $MoCl_5$, $FeCl_3$, and WCl_6 were synthesized by Croft's[8] and Rudorff's[9] methods by heating graphite-metal salt mixtures in a sealed ampoule in an atmosphere of chlorine or argon or under vacuum. Conditions for the synthesis of these compounds of different stages and their dependence of the graphite's type were described earlier.[15,16] Compounds of $CoCl_2$, $NiCl_2$, $MnCl_2$, $CuCl_2$, and $CrCl_3$ were prepared by chlorination of graphite and metal mixture. $FeCl_2$ LCG were obtained by reduction of $FeCl_3$ LCG by hydrogen at 400°.[16] Compositions, stages, identity periods, and thicknesses of the filled layers of initial LCG with metal chlorides are given in Table I.

Methods of Investigation. X-Ray studies have been performed both with a one-circle diffractometer "DRON-I" (Cu Kα radiation, Ni filter) and with a Debye-Scherer camera (diameter 114 mm, Cu Kα and Fe Kα radiation). Results are given in Table I.

Magnetic measurements have been performed with a magnetic balance by the Faraday method over the temperature range 4.2-300°K and in magnetic fields up to 7 kOe for Fe, Co, Ni, Mn, Cu, Mo, Cr, and W LCG. For some Fe LCG a hysteresis loop has been established at helium and room temperatures in weak fields.

Mössbauer Spectra. Fe LCG under investigation served as absorbers in conventional Mössbauer transmission experiments. The absorbers have been molded in plexiglass cells without any binder. The weighed amounts of compounds have been used which gave the density in iron 10-15 mg/cm^2. Mössbauer spectra have been taken on an electrodynamic spectrometer with a multichannel analyzer in a constant acceleration regime, the spectrometer being calibrated with α-Fe and sodium nitroprusside spectra at 300°K. Samples have been studied at 80 and 300°K, the external magnetic field of $H = 20$ kOe being normal to the γ-quanta beam and applied at 300°K. The field has been supplied by a permanent magnet system.[17] Mössbauer spectra of cobalt LCG were studied on samples containing the ^{57}Co isotope by an emission Mössbauer spectroscopy method on an apparatus with the moving standard potassium ferrocyanide absorber at room temperature.

Table II. The Products of Metal Chloride LCG Reduction by $NaBH_4$, $LiAlH_4$, and $Na-NH_3$

Initial metal chloride LCG	Reducing agent	Solvent	T, °C	Content, % C	H	M^a	B, Al, or N
$FeCl_3$ I stage	$NaBH_4$	H_2O	25	34.4	2.14	14.25	Traces
			100	35.8	2.6	15.4	No
	$LiAlH_4$	THF	25		1.1	10.5	3.2
			66	52.7	3.73	12.1	8.9
	Na	NH_3	−30	54.0	0.4	9.8	0.8
$FeCl_3$ II stage	$NaBH_4$	H_2O	25	48.15	0.5	17.6	
			100	48.35	1.3	16.2	Traces
	$LiAlH_4$	THF	25	51.1	1.7	9.6	6.8
			66	54.3	1.4	9.4	6.0
$NiCl_2$ II stage	Na	NH_3	−30	54.2	1.4	17.5	1.6
$MoCl_5$ II stage	Na	NH_3	−30	66.0	0.6	19.0	1.7

[a] M = Fe, Ni, or Mo.

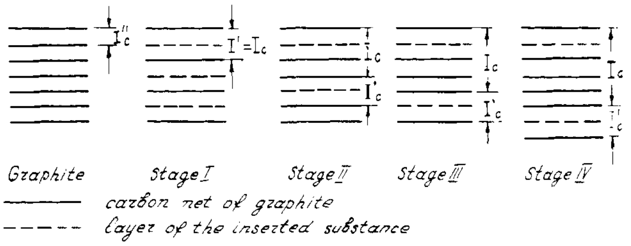

Figure 2. Stages of the lamellar compounds of graphite.

Isomeric shifts (IS) in this paper are given as related to sodium nitroprusside, at 300°K. The LCG composition has been determined by the spectra areas at 80°K assuming the constancy of f'.

Reduction by Hydrogen. The metal chloride LCG were heated in hydrogen flow at 300° for 4 hr; then the temperature was raised to 400-800° and the heating was continued. In all cases it was found that the metals leave the interlayer space of graphite and the samples obtained contain separate phases of the metal and of the graphite.

An exception was the reduction of the $MoCl_5$ LCG by H_2 at 250-400°. In this case the X-ray diffractograms show lines of the Mo LCG, besides those of metallic Mo and free graphite.

Reduction by Sodium Borohydride. Four grams of $NaBH_4$ was dissolved in 200 ml of an aqueous or alcoholic solution of KOH and 1.5 g of metal chloride LCG was added on stirring in an argon flow. The reaction mixture was stirred at room temperature or at reflux for 4 hr. The solid was washed with 10% HCl, water, acetone, and ether and dried at 120° for 10 hr. The composition of resulting compounds is given in Table II.

Reduction by Lithium Aluminum Hydride. One gram of metal chloride LCG was added to 50 ml of a 10% solution of $LiAlH_4$ in tetrahydrofuran (THF) in argon flow. The

Table III. The Products of Metal Chloride LCG Reduction by Lithium Diphenylide

Metal LCG	Stage	Way of treatment[a]	Metal content, %	
			Analysis	Magnetic data
Fe	I	A	4.6	1.5
		B	27.4	28.0
Fe	II	A	1.9	1.5
		B	34.8	30.0
Co	I	A	13.1	7.2
		B	28.4	22.7
Ni	II	A	7.3	4.8
		B	21.0	21.0
Mo	II	B	27.8	*b*
Mo	III	B	19.1	*c*
Mo	IV	B	16.7	*d*
W		B	22.4	*e*

[a] Key: (A) reduced, washed with THF and dried under vacuum; (B) as in (A) and then treated with ethanolic HCl, dried under vacuum and heated at 400–600°. [b] Diamagnetic $\chi = -0.96 \times 10^{-6}$ cgsm/g. [c] Diamagnetic $\chi = -1.26 \times 10^{-6}$ cgsm/g. [d] Diamagnetic $\chi = -1.49 \times 10^{-6}$ cgsm/g. [e] Diamagnetic $\chi = -1 \times 10^{-6}$ cgsm/g.

mixture was stirred for 4 hr at room temperature (or at reflux). The residue was filtered, washed with dry THF, treated with 10% HCl, washed with water, and dried at 120° for 10 hr. The composition of resulting compounds is given in Table II.

Reduction by Sodium in Liquid Ammonia. The suspension of 1 g of metal chloride LCG in 100 ml of liquid ammonia was added to 200 ml of a 0.04 *M* solution of sodium in liquid ammonia at −70° in a dry argon flow. The mixture was stirred for 4 hr at −70°, filtered off, and washed with liquid ammonia. The residue was divided into three parts. The first part was dried under vacuum at room temperature; the second was treated with ethanol and dried at 120° for 10 hr; the third part was treated in the same way as the second and then heated in hydrogen or argon flow at 400–600°. The composition of resulting compounds is given in Table II.

Reduction by Aromatic Anion–Radicals. Three grams of metal chloride LCG was added to 200 ml of a 0.1 *M* solution of anion-radical in THF. The mixture was stirred for 2 hr at room temperature and left in the refrigerator for 3 days. The residue was then filtered off, washed with dry THF, and divided into three parts. The first part was dried under vacuum at room temperature for 8 hr. The second part was treated with alcohol, boiled in a mixture of alcohol and 15% HCl (1:1), and then dried under vacuum for 10 hr at 120°. The third part was treated in the same way as the second and then heated in hydrogen or argon flow at 400–600°. The composition of resulting compounds is given in Table III.

Magnetic Properties of LCG with Metals. Magnetic properties of Mo LCG have shown that all reduced compounds are diamagnetic (Table III), although the starting $MoCl_5$ LCG are highly paramagnetic. It indicates the absence of either free atomic Mo or starting $MoCl_5$ LCG.

The susceptibility value of reduced compounds is one order of magnitude less than of the initial graphite and is equal to 1×10^{-6} cgsm/g. The latter value can be related to the formation of Mo complexes with a graphite aromatic carbon net.

Heating of the Mo LCG samples in an argon flow at 600° results in a diamagnetism increase up to a value close to that of graphite. This fact agrees with X-ray data which indicate that compounds decompose on heating with formation of metallic molybdenum and graphite phases.

The magnetic behavior of Fe LCG depends on the form of reduced iron which can be present in a compound: (a) as monolayers between graphite layers, (b) as complexes, and (c) as three-dimensional aggregates or clusters. Type a LCG of the I stage are expected to be ferromagnetic, the saturation moment coinciding with that of a bulk iron and the Curie point being lower than that of a bulk iron, but in cases in which the iron monolayers are separated by two or more layers of graphite (LCG of stages II and higher) the interaction between adjacent layers should be significantly weaker. In the last case one can expect that even if such iron layers do not transform to the ferromagnetic state the samples should nevertheless act as superparamagnetics. Their saturation moment will correspond to that of metallic iron due to the strong interaction within the layer.

These assumptions are based on our previous investigation,[18-20] where the sign of an exchange interaction between $FeCl_3$ layers separated by one graphite layer has been shown to be the same as for the pure salt. If the layers are separated by two or more graphite layers the interaction between them becomes negligibly weak and the magnetic behavior of such systems is governed by the interactions within the layer.

The compounds of type b, where iron atoms form some kind of complexes with the carbon net of graphite, could be either diamagnetic or paramagnetic.

If iron atoms gather into three-dimensional clusters (type c) the compound will be then ferromagnetic or superparamagnetic. As clusters enlarge, their saturation moment and Curie point will approximate values characteristic for a bulk α-Fe.

A study of the magnetic properties of Fe LCG obtained by the action of different reducing agents has shown the reducing conditions to have a marked effect on the properties of resulting compounds.

In the case of samples obtained on reduction by lithium diphenylide, the magnetic moment depends on the field nonlinearly and the saturation moment is registered in the fields between 3 and 7 kOe. Such behavior is typical for ferromagnetic materials. The data of Table III show that for some samples the Fe content determined from magnetic data is close to that found by elemental analysis. It demonstrates that iron is present mainly in the ferromagnetic state.

To ascertain the form in which iron is present in these samples, as aggregates or in the superparamagnetic state, hysteresis loops have been measured at 295 and 4.2°K (Figure 3a,b). Susceptibility in weak fields for Fe LCG of stage II (obtained on reduction by lithium diphenylide with subsequent heating in hydrogen) is completely independent of the temperature (Figure 3c), but susceptibility for Fe LCG of the stage I sharply increases at helium temperature (Figure 3d). The saturation moment of a sample also increases almost at a ratio of 1.5. It shows that in the samples there are very small particles (clusters) in the superparamagnetic state.

Thus in Fe LCG obtained by reduction by lithium diphenylide, iron is in the form of both large Fe particles (aggregates) and very small superparamagnetic clusters.

Magnetic susceptibility measurements of Fe LCG obtained on reduction by sodium in liquid ammonia and by $LiAlH_4$ have shown the iron is mainly in paramagnetic state, the proportion of ferromagnetic iron being insignificant.

We have measured the magnetic susceptibility of these compounds in the region from 1.5 to 300°K (Figure 4). The magnetic moment of iron $\mu = 4.77$ BM is determined from the value of the paramagnetic part of the susceptibility at 1.5–30°K. Such atomic magnetic moment values can correspond either to Fe(+2) or Fe(0). It has been shown that $FeCl_2$ LCG transforms into the ferromagnetic state at 15°K,[19] but in our case it is not so down to 1.5°K. We

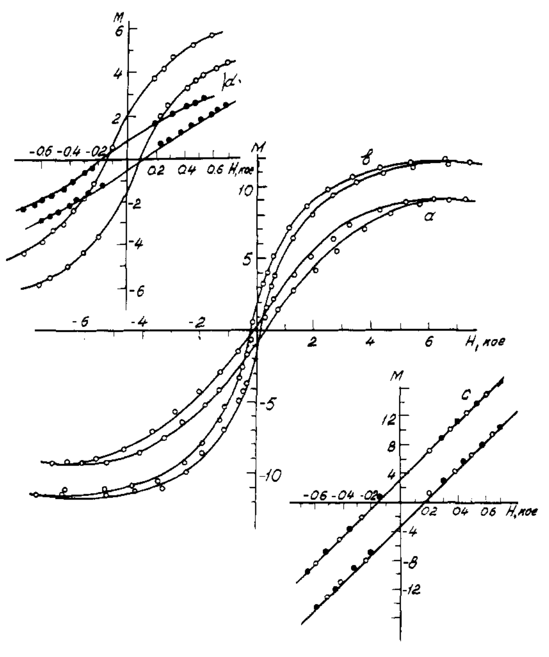

Figure 3. Magnetization curves at 295 (a) and 4.2°K (b) of Fe LCG of stage I obtained on reduction by lithium diphenylide. Moment *vs.* field in weak fields for LCG of stage II (c) and of stage I (d) before (●) and after (○) heating in hydrogen.

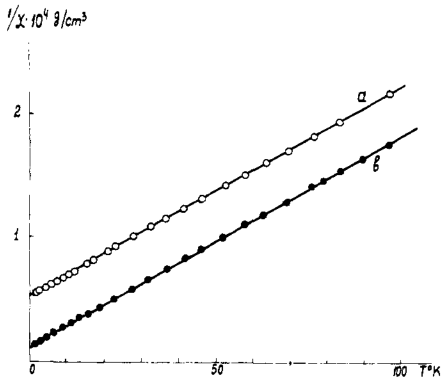

Figure 4. Temperature dependence of the reverse susceptibility for Fe LCG obtained on reduction by sodium in liquid ammonia (a) and lithium aluminum hydride (b).

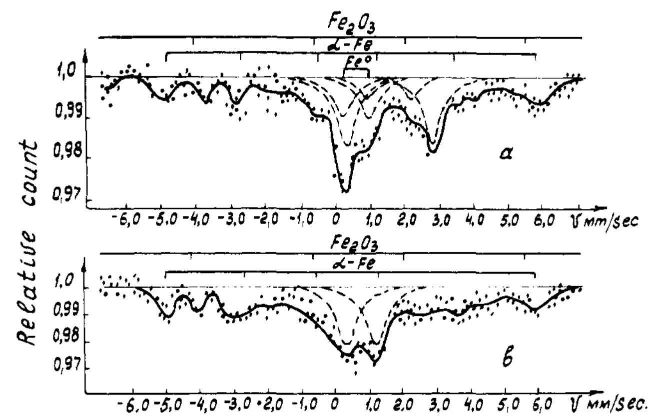

Figure 5. Mössbauer spectra of Fe LCG obtained on reduction by lithium diphenylide (T 80°K): (a) stage I, (b) stage II.

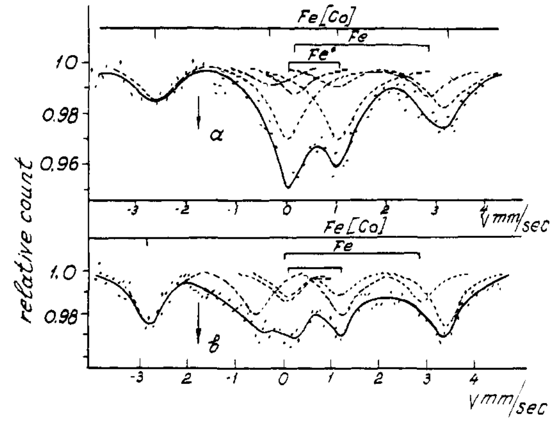

Figure 6. Mössbauer spectra of ^{57}Co LCG of stage II obtained on reduction by lithium diphenylide before (a) and after (b) heating in hydrogen.

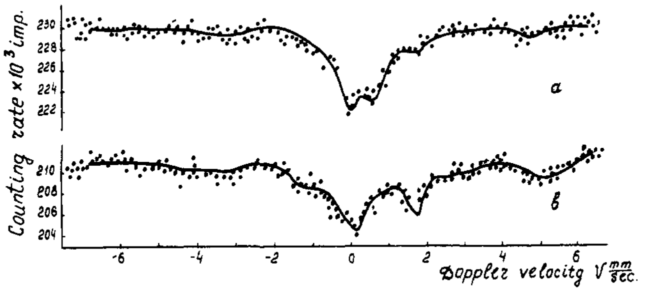

Figure 7. Mössbauer spectra of Fe LCG of stage I obtained on reduction by Na-NH$_3$: (a) 300°K (b) 80°K.

suggest that in these compounds paramagnetism is associated with Fe(0) complexes. The other possibility, the formation of free atomic iron, is excluded by Mössbauer spectra data (*vide infra*).

A study of the magnetic properties of Co and Ni LCG obtained by reduction of CoCl$_2$ and NiCl$_2$ LCG by lithium diphenylide has shown that these compounds are similar to LCG with Fe in their magnetic behavior, and it can denote that in these cases some metal complexes with graphite are also formed.

Mössbauer Spectroscopy Study. Mössbauer spectroscopy has been applied to Fe and ^{57}Co LCG. The results are given in Table IV and some typical spectra are given in Figures 5-7.

Mössbauer spectra investigation of Fe LCG obtained by reduction of FeCl$_3$ LCG by aromatic anion-radicals has shown that the spectra are rather complex, and no distinct HFS is found even at 80°K. A great number of magnetically ordered forms can be seen which are obviously in the superparamagnetic state. The main feature of a paramagnetic part of the spectra is the doublet with the parameters IS 0.60 mm/sec and QS 0.90 mm/sec which amounts to 20-40% of the spectrum area. This doublet is observed after reduction of both FeCl$_3$ LCG (of the stage I and II) and FeCl$_2$ LCG and in emission spectra of ^{57}Co LCG. Therefore it cannot be assigned to the incompletely reduced FeCl$_3$ LCG. This doublet cannot be assigned to free iron in cluster or atomic state either as its IS does not correspond to that of α- and γ-iron. Thus this doublet could be assigned to complexes of zero valent iron, perhaps complexes with graphite.

To remove the aggregated portion of iron which separated from the graphite layers, samples were washed with a mixture of alcohol and hydrochloric acid. After washing, the doublet assigned to complexes of iron remained in all cases. Further heating in a hydrogen flow at 500-600° led to the formation of α-Fe phase as the main form of iron.

Therefore the Mössbauer spectra indicate the formation of some zero-valent iron compounds, but one cannot exclude the possibility of the presence of complexes of iron with THF and/or biphenyl which could penetrate the interlayer spaces of graphite. To check this hypothesis we have

Table IV. Mössbauer Spectra Parameters of the Reduced LCG

Sample	Fe complex (narrow doublet)					High spin Fe^{2+} (wide doublet)								Magnetic forms (α-Fe)				
	300°K		80°K			300°K				80°K				300°K		80°K		
	IS (mm/sec)	QS	IS (mm/sec)	QS	$f'(80°K)/f'(300°K)$	IS (mm/sec) 1	IS (mm/sec) 2	QS (mm/sec) 1	QS (mm/sec) 2	IS (mm/sec) 1	IS (mm/sec) 2	QS (mm/sec) 1	QS (mm/sec) 2	IS (mm/sec)	H_{loc}, kOe	IS (mm/sec)	H_{loc}, kOe	$f'(80°K)/f'(300°K)$
$FeCl_2$ LCG						1.33	1.33	0.90	1.89	1.48	1.50	1.12	2.04					
$^{57}CoCl_2$ LCG										1.38	1.42	1.20	2.14					
α-Iron														0.37	330	0.46	336	
$FeCl_3$ LCG reduced by H_2 at 550°						1.25		0.80		1.43		1.00		0.26	330	0.40	333	
Reduction by lithium diphenylide																		
(a) $FeCl_3$ LCG stage I	0.59	0.45	0.62	0.90	1.65					1.54	1.62	1.51	2.44			0.51	341	
(b) $FeCl_3$ LCG stage II	0.68	0.71	0.83	0.85	1.60													
(c) $FeCl_2$ LCG stage I	0.64	0.81	0.60	0.81	1.80											0.51	337	
(d) $^{57}CoCl_2$ LCG			0.55	1.00							1.54		2.70			0.41	318	
(e) $FeCl_3$ LCG stage II (H_{ext} = 20 kOe)														0.51	337 ± 15			
(f) mixture $FeCl_3$ with graphite	0.61	0.71	0.72	0.73	3.5									0.20	280 ± 15			
Reduction by lithium diphenylide, washing and subsequent heating in H_2 at 500–600°																		
(a) $FeCl_3$ LCG stage I	0.37	0	0.5											0.37	329	0.52	342	1.2
(b) $FeCl_3$ LCG stage II	0.5	0	0.4											0.34	329	0.48	339	1.0
(c) $FeCl_2$ LCG stage I	0.4	0	0.45											0.34	329	0.54	342	1.0
(d) $FeCl_3$ LCG stage I H_{ext} = 20 kOe														0.36	312			
(e) $FeCl_3$ LCG stage II H_{ext} = 20 kOe	0.48 (19 kOe)													0.32	314			
Reduction by other reducing systems																		
(a) $FeCl_3$ LCG stage I by Na–NH_3	0.58	0.64																
(b) $FeCl_3$ LCG stage I by $LiAlH_4$ in THF	0.61	0.66	0.73	0.66	2.5													
(c) $FeCl_3$ by $LiAlH_4$ in THF			0.50	0.50														
(d) $FeCl_3$ LCG stage I by $NaBH_4$ in H_2O			0.74	0.73														

studied the reduction of $FeCl_3$ LCG by another agent, lithium aluminum hydride. The same solvent, THF, is used and as aromatic compound only graphite is present. The main component of the Mössbauer spectra (Table IV) of Fe LCG prepared in this way is a doublet of "Fe(0) complex" (65–70% of the spectrum area at 80°K) with parameters close to those of Fe complex formed on reduction by lithium diphenylide (Table IV). Besides that a singlet of $FeCl_3$ LCG (10%) can be found in the spectrum. Reduction of free $FeCl_3$ by lithium aluminum hydride in THF results in different Mössbauer spectrum.

Reduction of $FeCl_3$ LCG by sodium boron hydride also gives 35% of "Fe(0) complexes" and a doublet of a high spin Fe(+2) is also present in the spectrum (Table IV). In these last experiments there were no aromatic hydrocarbons in the system except graphite, the solvents were different (alcohol, water), but the same doublet was observed which had been previously assigned to "Fe(0) complex" with graphite.

Mössbauer spectra of Fe LCG obtained after reduction of $FeCl_3$ LCG by sodium in liquid ammonia were measured at 300 and 80°K and are shown in Figures 6 and 7. These spectra also contain the doublet similar to that of the "Fe(0) complex" discussed above. Besides that a part of iron atoms of LCG of the stage I and II enters into the superparamagnetic clusters. Actually on cooling to 80°K clusters are partially stabilized, and magnetic HFS relating to the largest clusters begins to appear.

Consider now in greater detail the structures which produce the magnetic HFS in Mössbauer spectra. On reduction of $FeCl_3$ LCG in mild condition, along with the paramagnetic component in the Mössbauer spectra, there is also observed the absorption in the wide range of rates with the weakly resolved HFS at 80°K (Figure 5). Thus in the case of Fe LCG (obtained on reduction of $FeCl_3$ LCG stage II by lithium diphenylide) magnetic HFS does not appear at all at 300°K, although in the external magnetic field of 20 kOe the very scattered component is also observed along with the absorption in the spectrum's central part. At 80°K already two sufficiently distinct broadened line systems of magnetic HFS have been observed.

Such behavior is specific for systems of superparamagnetic particles with considerable scatter in dimensions and magnetic moments.[21-23] Magnetic moments of only the largest particles, which are alone responsible for the scattered HFS in Mössbauer spectra, are stabilized at 300°K in a magnetic field of 20 kOe. The main portion of particles remains in the paramagnetic state. On cooling down to 80°K there occurs the more complete stabilization of magnetic moments of the majority of particles.

Thus spectra of Fe LCG obtained on reduction by lithium diphenylide (Figure 5) can be roughly interpreted as conforming to three types of structures: (a) superparamagnetic particles of α-iron (H_n = 337 kOe), (b) clusters in which the close surrounding of Fe atoms differs from that of α-Fe (In particular the structure with monolayers of iron atoms between graphite carbon nets corresponds to such a situation. The magnetic moment of iron atoms decreases for such clusters (H_n = 280 kOe)), (c) the doublet component of graphite complex with iron.

Discussion

One should consider three possible structures of LCG with metals: (a) formation of metal complexes with graphite, (b) formation of monolayers of metal atoms between graphite layers, (c) formation of aggregates of metal atoms between graphite layers.

Consider now separately the results obtained on reduction of different metal chloride LCG.[24]

Table V. Found and Computed Thicknesses of Filled Layers of the Metal Graphite Lamellar Compounds

Graphite lamellar compounds with metals	Thickness of filled layer (Å)			
		Calcd for compounds of the type		
	Found	van der Waals	Olefinic	Arenic
Fe	5.8–5.9	5.89	4.0–4.2	
Co	5.6–5.8	5.85	4.0–4.2	
Ni	5.7–5.8	5.97	4.0–4.2	
Mn	5.7–5.9	5.83	3.9–4.0	
Cu	5.7–5.9	5.91		
Mo	3.7–4.0	6.15	4.5–4.7	3.5

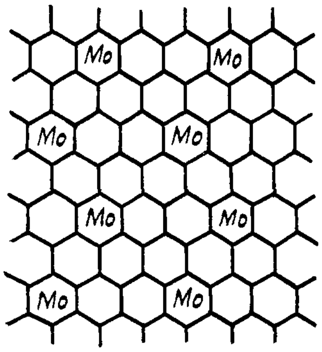

Figure 8. "Ideal" arrangement of molybdenum atoms relative to the carbon net of graphite in LCG with Mo.

The Chromium, Molybdenum, and Tungsten LCG. $MoCl_5$, WCl_6, and $CrCl_3$ LCG are reduced to the zero-valent state under the action of different reducing agents.

The reduction of $MoCl_5$ LCG of the stage II, III, and IV by the electronic reducers (sodium naphthalenide, lithium diphenylide, and sodium in liquid ammonia) results in a considerable spacing (identity period) decrease amounting to 5.5 Å (Table I). The distinctive peculiarity of the resulting Mo LCG is its filled layer thickness from 3.7 to 4.0 Å (Table V) regardless of reducing agent and the stage of initial $MoCl_5$ LCG. This value is much smaller than the filled layer thickness calculated in an additive fashion by summing the doublet atomic radius of molybdenum and the van der Waals thickness of the graphite net (2(1.40) + 3.35 = 6.15 Å). Such a significant discrepancy (6.15 − 3.80 = 2.35 Å) points out a chemical interaction of Mo atoms with the graphite net. It should be noted that the measured thickness for the filled layers (3.7-4.0 Å) is close to twice the benzene-molybdenum distance in arenic complexes of molybdenum (3.5 Å). This shows that the structure of Mo LCG follows the pattern of bisarenic molybdenum π-complexes and that graphite behaves in this LCG as an aromatic π-ligand.

For the formation of such bisarenic structures the shift of graphite carbon nets is necessary resulting in a carbon atom-on-atom symmetrical position of two nets separated by a metal atom layer. Such shift of graphite nets requires a small energy of 1-2 kcal/(g atom C) and proceeds easily even on LCG formation with alkali metals and acids.[6]

The method of synthesis of Mo LCG, *i.e.*, the reduction of $MoCl_5$ LCG, results in compounds whose composition correspond to 10 carbon atoms per each Mo atom in each graphite layer. Proceeding from this and assuming the regularity of Mo atoms distribution in the interlayer space of graphite, the possible ideal model for distribution of Mo atoms in a layer may be given (Figure 8). Here each six-membered ring participating in π-complex formation is surrounded by six "free" rings. However, the X-ray data available at present (not including the lattice parameters along "*a*" and "*b*" axes) do not yet permit us to assign the actual distribution of molybdenum atoms in a layer.

Data on magnetic susceptibility might serve as a confirmation of a sandwich-like structure of Mo LCG since $MoCl_5$ LCG are paramagnetic and free atomic Mo should be paramagnetic but Mo LCG with a bis π-arenic sandwich-like structure should be diamagnetic. The value of the diamagnetic susceptibility of Mo LCG is one order smaller than that of the initial graphite (Table III), which agrees with an assumption of molybdenum π-complex formation with the graphite carbon net.

We failed to obtain the X-ray diffractograms of W and Cr LCG since the initial compounds (with metal chlorides) were apparently highly disordered. The study of the magnetic properties of W LCG has shown that these compounds are diamagnetic although atomic tungsten should be paramagnetic. The susceptibility of the reduced compound is -0.8 to -1.1×10^6 cgsm/g. A comparison of susceptibilities of tungsten and molybdenum LCG shows that these values are close to one another. Thus it can be supposed that LCG with tungsten and molybdenum have similar structures; *i.e.,* W LCG is a π-complex of bisarenic type where graphite nets act as aromatic ligands.

Chromium should form compounds of a similar type. The study of the susceptibility of Cr LCG has shown that they are slightly paramagnetic and this can be related to the presence of impurities of either chromic oxides or some bis graphite chromium cations.

The Iron LCG. The more complex situation is in the case of reduction of $FeCl_3$ LCG and $FeCl_2$ LCG. Under the action of such reducing agents as aromatic anion-radicals, sodium in liquid ammonia, and lithium aluminum hydride, reduction of the salt without escape of iron from the interlayer space occurs. Fe LCG of stages I and II have been obtained where the filled layer thickness is 5.8-6.0 Å (Table V), which corresponds to the sum of van der Waals dimensions. In graphite π-complexes of allylic or olefinic types the filled layer thickness should be equal to 4.0-4.4 Å. In some X-ray diffractograms of LCG of the stage I there are lines which could be assigned to the spacing of 4.4 Å; however, these lines are badly reproduced. Thus the observed X-ray pattern of Fe LCG clearly shows the presence of metal atom monolayers between graphite layers with the van der Waals interaction between them. However, this pattern does not reject the formation of other types of compounds.

The data of Mössbauer spectra turned out to be much more efficient in this respect. It appeared that in the overwhelming majority of samples the iron was present in layers in two forms: (a) magnetically ordered form, ferromagnetic and superparamagnetic iron, and (b) paramagnetic form (doublet, IS = 0.6 mm/sec, QS = 0.9 mm/sec). This doublet is registered on reduction of both $FeCl_3$ and $FeCl_2$ LCG under the action of different reducing agents such as aromatic anion-radicals, sodium in liquid ammonia, and lithium aluminum hydride. One can assume that this doublet is related not to atomic iron but to iron associated in a "weak complex" with graphite since its IS differs essentially from that of iron in α and γ forms. The area of the doublet shows that the quantity of iron in this form is 20-40% of the total quantity of iron in the case of reduction by lithium diphenylide and up to 90% (together with paramagnetic clusters) in the case of reduction by sodium in liquid ammonia. Magnetic measurements also agree with those data and demonstrate that the main part of the iron in these compounds is in the paramagnetic state. A study of the magnetic susceptibility changes with temperature has made it possible to determine the magnetic moment of iron in "iron complexes" which appears to be equal to 4.8 BM and corresponds to four unpaired electrons.

The data available do not permit determination of the exact nature of such complexes and only some assumptions can be made. On the basis of magnetochemical and Mössbauer spectroscopy data one can postulate a 4s electron density transfer from Fe(0) ($3d^64s^2$) to graphite in this "complex," the iron atom thus obtaining a structure close to $3d^64s^{0.35}$.

The Cobalt, Nickel, Manganese, and Copper LCG. Reduction of $CoCl_2$, $NiCl_2$, $MnCl_2$, and $CuCl_2$ LCG by anion-radicals results in the reduction of salt to metal without its escape from graphite. The spacings (identity periods) of reduced compounds of the stages I and II are 5.6-5.8 and 9.3-9.6 Å, respectively. The thickness determined for a filled layer of Co, Ni, Mn, and Cu LCG (5.6-5.8 Å), similar to LCG with iron, corresponds to the sum of the van der Waals thickness of the graphite net and the metal atom diameter. However, one cannot rule out a possibility for a part of metal atoms in these compounds to form complexes with graphite nets of the same type as in the case of iron. Such formation of complexes has been confirmed for Co LCG. In this case the use of the ^{57}Co isotope transformation into ^{57}Fe as a result of K-capture enables Mössbauer spectroscopy to be applied. The same doublet as in the case of graphite compounds with iron is registered in the paramagnetic part of the Mössbauer spectra of ^{57}Co LCG (Table IV). The doublet can be assigned to the cobalt complexes (similar to iron complexes) with some kind of interaction between Co atoms and graphite nets.

One can also suppose that at least in the case of Ni LCG there are complexes with graphite similar to iron complexes since a discrepancy in nickel content determined on the basis of magnetic data (ferromagnetic nickel) and chemical analysis (total nickel content) is observed. The same regularity is registered as in the case of iron LCG; the difference in nickel content decreases when passing from reduced compounds to the washed ones and almost completely vanished in heated samples.

As far as Cu LCG are concerned, magnetic measurements are of little value since both copper and graphite are diamagnetic. The X-ray data show that both copper and its oxides are present in those LCG.

Investigation of magnetic susceptibility of Mn LCG has shown that the compounds are paramagnetic (1.07×10^{-5} cgsm/g in the case of LCG with 13% Mn and 2.34×10^{-5} cgsm/g in the case of LCG with 27% Mn). However, a contamination by manganese oxides (according to X-ray data) prevents the determination the magnetic moment of manganese atoms.

We believe that the LCG prepared should have some interesting catalytic properties. Firstly, these compounds contain the metal in a free atomic state or in the form of weak complexes, the graphite layer preventing the aggregation of the metal atoms to the bulk metal. Secondly, the very high conductivity of the graphite layers should facilitate electron transfer reaction. Finally, the selectivity could be due to the fixed distances between the layers which are filled by metal atoms.

Indeed we have found some examples of catalytic activity of the compounds.[25] For example nickel LCG is a selective catalyst for the formic acid and alcohol dehydrogenation without dehydration: formic acid decomposed to CO_2 and H_2, ethanol gives acetaldehyde, isopropyl alcohol-acetone, cyclohexanol-cyclohexanone, etc.

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Octahedral and Tetrahedral Solvates of the Aluminum Cation. A Study of the Exchange of Free and Bound Organophosphorus Ligands by Nuclear Magnetic Resonance Spectroscopy

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Abstract: The existence of octahedral solvates of the Al^{3+} cation with trialkylphosphates, phosphonates, dialkyl hydrogen phosphites, and a tetrahedral solvate of hexamethylphosphorotriamide (HMPA) is shown by their ^{27}Al and ^{31}P NMR spectra in nitromethane. The kinetics of the exchange of free (A*) and bound (A) ligand molecules, $AlA_6{}^{3+}$ or $AlA_4{}^{3+} + A^* \rightarrow AlA_5A^{*3+}$ or $AlA_3A^{*3+} + A$, have been investigated. Sharply contrasting conclusions are reached for hexa- and tetracoordinated aluminum(III). The rate laws are respectively zero and first order in free ligand for octahedral and tetrahedral solvates. These data are consistent with a dissociative and an associative substitution mechanism, respectively. This mechanistic change is accompanied by a strong decrease of the activation enthalpies and entropies. Typical values are $k_{25°} = 5.1$ sec^{-1} and 4.8×10^3 M^{-1} sec^{-1}, $\Delta H^{\ddagger} = 19.8$ and 7.7 kcal mol^{-1}, $\Delta S^{\ddagger} = 6.9$ and -10.2 eu for Al(dimethylmethylphosphonate)$_6{}^{3+}$ and $Al(HMPA)_4{}^{3+}$, respectively. Aqueous solutions of these solvates were also examined by ^{27}Al NMR; separate resonances are observed for the whole range of the various species: $AlA_i(H_2O)_{6-i}{}^{3+}$, $i = 0$–6.

A point of interest in the study of dissolved ions and their effect on the structure of the surrounding medium is the constitution of the first solvation shell. In this respect, NMR spectroscopy has proved to be an invaluable tool since, in electrolyte solutions, the presence of ions modifies the charge distribution in molecules of the solvent coordination sphere and therefore the shielding of their nuclei. The most direct method uses systems in which the exchange of solvent molecules between the various species is sufficiently slow that separate resonances are observed for the free and bound solvent, S_f and S_b, respectively.[1] However, the scope of this method is sharply restricted to a few ion-solvent systems on account of the NMR time scale, and few cations can be studied in this manner. Al^{3+} solvation shells have been extensively studied in the past in a variety of organic solvents by proton NMR.[2-7] Some extension of the possible cation-solvent systems can be hoped for on account of the larger chemical shifts of other nuclei in the solution. In 1969 and 1971, we proposed using ^{31}P[8] and ^{13}C[9] spectroscopy of organophosphorus solvents, all containing the phosphoryl P=O solvating link: trimethyl- (TMPA) and triethylphosphates (TEPA); dimethylmethyl- (DMMP) and diethylethylphosphonates (DEEP); dimethyl hydrogen phosphite (DMHP); hexamethylphosphorotriamide (HMPA).

The present paper is chiefly devoted to the study of the NMR properties of the aluminum cation itself in the same series solvents. Aluminum-27 is an attractive nucleus on account of its high sensitivity and of a 100% isotopic abundance. However, its spin number, $I = 5/2$, results in a nuclear quadrupolar moment strongly interacting with electric field gradients which originate in an asymmetrical arrangement of the ligands around the Al^{3+} cation. Therefore cubic symmetrical complexes such as $Al(H_2O)_6{}^{3+}$ are necessary for observation of sharp lines. Any deviation from pure cubic symmetry brings forth a characteristic line broadening, as it was shown[10] for the ion pair $Al(H_2O)_5(HSO_4{}^-)^{2+}$.

Our previous studies[11-14] only used aqueous solutions of the Al^{3+} cation in an organophosphorus cosolvent A, resulting in the presence of several unsymmetrical solvates: $S_i \equiv AlA_i(H_2O)_{6-i}{}^{3+}$, $i = 0$–6. More simple systems are therefore, desirable for an initial study. We then planned to study the aluminum cation coordinated to identical organophosphorus ligands; octahedral $AlA_6{}^{3+}$, $3ClO_4{}^-$ and tetrahedral $Al(HMPA)_4{}^{3+}$, $3ClO_4{}^-$ solvates were then prepared in the solid state[15] and dissolved in nitromethane, an inert solvent.[16] Such a medium also allowed an easier kinetic study by permitting addition of variable amounts of the free ligand. A significant comparison of substitution reactions of octahedral and tetrahedral complexes of the same cation is then possible. In a second step, aqueous solutions of these