Solid-state mechanochemical synthesis of tris(4-imino-2-pentanonato)chromium, $Cr[CH_3C(NH)CHC(O)CH_3]_3$

*A. P. Borisov, L. A. Petrova, T. P. Karpova, and V. D. Makhaev**

Institute of New Chemical Problems, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (095) 938 2156

Tris(4-imino-2-pentanonato)chromium was prepared by solid-state synthesis under conditions of mechanical activation of a mixture of chromium(III) chloride and sodium 4-imino-2-pentanonate and characterized by IR spectroscopy, X-ray diffraction, and electronic absorption spectroscopy.

Key words: chromium complexes, acetylacetoneimine, mechanochemical synthesis.

The preparation of derivatives of chromium acetylacetonate substituted at the carbonyl group is a difficult problem because of hydrolysis of the ligands in aqueous solution, which results in the formation of chromium acetylacetonate instead of the desired compound.[1] Certain compounds of this class, *e.g.*, complexes with aminoketonate ligands, containing bulky phenyl and benzyl groups[2] and chromium monothioacetylacetonate[3] have been synthesized using nonaqueous solvents.

We showed earlier that mechanical activation of mixtures of a 3d-metal chloride and sodium acetylacetonate led to solid-state interaction between them with the formation of the corresponding transition metal acetylacetonate.[4] It was of interest to investigate the possibility of using the method of solid-state mechanochemical synthesis to obtain chromium acetylacetonate derivatives substituted at the carbonyl group. In this communication we report the results of the investigation of the interaction of chromium(III) chloride with sodium 4-imino-2-pentanonate (acetylacetoneimine) under conditions of mechanical activation.

Experimental

Mechanical activation of the reagents was carried out on a vibration mill designed at the INCP RAS (*cf.* Ref. 5). The working frequency of the mill is 12 Hz, the amplitude of vibrations is 11 mm.

IR spectra were recorded on a UR-20 spectrophotometer in the 400—4000 cm^{-1} range. Samples were prepared as suspensions in nujol (capillary layer between KBr plates). Electronic absorption spectra were recorded on a Specord UV-VIZ spectrophotometer (solution in chloroform). Diffractograms of powder samples were registered on a DRON-2 diffractometer (Cu-Kα radiation).

Anhydrous crystalline chromium(III) chloride ("chemically pure" grade) was used without additional purification.

Sodium 4-imino-2-pentanonate (sodium salt of acetylacetoneimine), NaACIM. Acetylacetoneimine[6] (27.0 g; 0.27 mol) was added to a solution of sodium isopropoxide prepared from 5.7 g (0.25 mol) of metallic sodium and 150 mL of abs. 2-propanol in small portions to avoid vigorous heating of the reaction mixture. A yellowish clear solution was obtained. The solvent was removed *in vacuo* at ~ 20 °C, the residue was dried *in vacuo*, and the temperature was gradually increased from ~20 °C to 100 °C. A pale-brown powder was obtained. The yield of NaACIM was 27.8 g (92 %). Found (%): N, 10.6; Na, 19.0. C_5H_8NNaO. Calculated (%): N, 11.6; Na, 19.0.

Tris(4-imino-2-pentanonato)chromium(III), $Cr[CH_3C(NH)CHC(O)CH_3]_3$ ($Cr(ACIM)_3$). A steel reactor (volume 70 cm^3) was charged with 0.22 g (1.4 mmol) of chromium(III) chloride, 0.56 g (4.6 mmol) of NaACIM, and 30 steel balls 12.3 mm in diameter (225 g) in an atmosphere of dry nitrogen. The reactor was hermetically sealed and the reaction mixture was mechanically activated for 30 min. After completion of the process a portion of the reaction mixture (a red-gray powder) was withdrawn for physicochemical investigations. The rest (0.21 g) was placed in a sublimation apparatus and heated *in vacuo* (~1 Torr). The sublimation of the product started at 150 °C, and the main part of the product was sublimed as red-brown needle-like crystals at 210—215 °C. The yield of $Cr(ACIM)_3$ was 0.09 g (68 %), m.p. 249 °C. Found (%): C, 52.06; H, 6.94; Cr, 15.0; N, 11.9. $C_{15}H_{24}CrN_3O_3$. Calculated (%): C, 52.02; H, 6.98; Cr, 15.0; N, 12.3.

Electronic absorption spectrum, λ/nm (log ε): 516(1.93); 346(3.84); 305(3.83); 266(3.96). Diffractogram, d/Å (I_{rel} (%): 9.12(41), 8.55(100), 6.75(9), 5.66(11), 4.29(19).

Results and Discussion

Mechanical activation of a mixture of $CrCl_3$ and NaACIM in a 1 : 3 ratio causes it to change color from

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2227—2229, December, 1994.

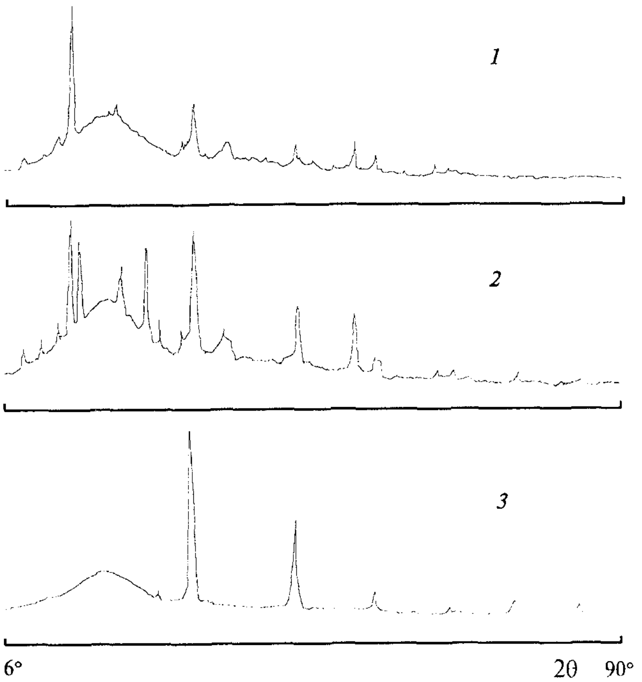

Fig. 1. Diffractograms of the reaction mixtures $CrCl_3$ + 3 NaACIM at various durations of mechanical activation, min: *1*, 1; *2*, 5; *3*, 10.

lilac to grayish-red. Instead of clear-cut reflections of $CrCl_3$ on the background of NaACIM in the starting mixture, the X-ray diffraction pattern of the reaction mixture contains characteristic reflections of NaCl and a broad band at about 2θ = 20°, which attests to the presence of a roentgenoamorphous phase (Fig. 1).

Sublimation of the reaction mixture *in vacuo* made it possible to isolate chromium tris(4-imino-2-pentanonate), $Cr(ACIM)_3$. No admixture of chromium acetylacetonate was found in the reaction products. Extraction of the activated mixture with benzene also makes it possible to isolate the target product. It should be noted, that extraction or heating *in vacuo* of a nonactivated mixture of the reagents (even after mixing on a vibrational mill for 1 min) does not allow one to obtain $Cr(ACIM)_3$.

The compound obtained is stable in air, is moderately soluble in chlorinated and aromatic hydrocarbons, and sublimes when heated at reduced pressure. Above 200 °C, $Cr(ACIM)_3$ sublimes also at atmospheric pressure.

Only one band of weak intensity at 516 nm, which corresponds to a d—d transition, and 3 intense charge-transfer absorption bands are observed in the electronic absorption spectrum of $Cr(ACIM)_3$. Comparing it with the spectrum of chromium acetylacetonate[7] shows that a hypsochromic shift of the longwave absorption band and an increase in the intensity of the charge-transfer bands are observed for the acetylacetoneimine derivative, which correlates with the relative position of the oxygen and nitrogen ligands in the spectrochemical series.

Table 1. Empirical assignment of absorption bands in the IR spectrum of $Cr(ACIM)_3$

ν/cm^{-1}	Assignment
3265 s	ν(NH)
2940 m	ν(CH)
2870 m	
1610 s	ν(C=O)
1525 s	ν(C=C)
1475 s	$\delta_{as}(CH_3)$
1420 m	δ(NH)
1385 s	$\delta_s(CH_3)$
1360 m	ν(C=N)
1220 s	ν(C—C) + ν(C—CH)
1180 s	δ(CH) in-plane
1020 s	$\rho_r(CH_3)$
950 sh	ν(C—CH3) + ν(C—O)
930 s	
825 m	δ(NH) out-of-plane
755 s	δ(CH) out-of-plane
685 m	δ cycle + ν(M—L)
655 m	
620 sh	ν(M—O) + ν(M—N)
605 s	
465 s	
425 m	

IR-spectroscopy data confirm the presence of acetylacetoneiminate ligands in the complex and are in good accordance with the data for other analogous complexes.[8] The empirical assignment of the absorption bands in the IR spectrum of $Cr(ACIM)_3$ is given in Table 1.

Compounds with acetylacetoneiminate ligands are known only for a few metals. Nickel(II) and copper(II) complexes were prepared in aqueous solutions.[6] Acetylacetoneiminate derivatives of scandium and some lanthanides were prepared using nonaqueous solvents.[9]

The results obtained in the present work show that the method of solid-state mechanochemical synthesis may be promising for obtaining other complex compounds with derivatives of β-diketones as ligands, whose synthesis in solutions is difficult to accomplish.

The present work was carried out as a part of Project No. 1.164 "Mechanochemical Synthesis of Complex Compounds" of The State Scientific and Technical Program "Ecologically Safe Processes in Chemistry and Chemical Technology" with the financial support of the Ministry of Science of the RF.

References

1. R. C. Mehrotra, R. Bohra, and D. P. Gaur, *Metal β-Diketonates and Allied Derivatives,* Academic Press, London, New York, 1978.
2. J. P. Collman and E. T. Kittleman, *Inorg. Chem.*, 1962, **1**,499.
3. V. I. Reutov, L. A. Lim, and N. P. Shapkin, *Zh. Obshch. Khim.*, 1993, **63**, 1428 [*J. Gen. Chem. USSR*, 1993, **63** (Engl. Transl.)].
4. A. P. Borisov, L. A. Petrova, and V. D. Makhaev, *Zh. Obshch. Khim.*, 1992, **62**, 15 [*J. Gen. Chem. USSR*, 1992, **62** (Engl.Transl.)].
5. K. G. Myakishev and V. V. Volkov, Preprint 89—12, Institute of Inorganic Chemistry, Siberian Branch of the RAS, Novosibirsk, 1989, 42 pp. (in Russian).
6. M. J. Lacey, *Austr. J. Chem.,* 1970, **23**, 841.
7. D. W. Barnum, *J. Inorg. Nucl. Chem.*, 1961, **21**, 221.
8. D. A. Thornton, *Coord. Chem. Rev.*, 1990, **104**, 173.
9. I. V. Andrienko and L. I. Martynenko, *Dokl. Akad. Nauk SSSR*, 1988, **298,** 870 [*Dokl. Chem.*, 1988, **298** (Engl. Transl.)].

Received May 12, 1994