

- Beckett, M. A., Cassidy, D. P. & Duffin, A. (1991). *Inorg. Chim. Acta*, **189**, 229–232.
- Darr, J. A., Drake, S. R., Hursthouse, M. B. & Malik, K. M. A. (1993). *Inorg. Chem.* **32**, 5704–5708.
- Davies, E. K. (1983). *SNOOPI. Molecular Plotting Program*. Univ. of Oxford, England.
- Karoulov, A. I. (1992). *ABSMAD. Program for FAST Data Processing*. Univ. of Wales, Cardiff, Wales.
- King, R. B. & Cloyd, C. J. Jr (1975). *Inorg. Chem.* **14**, 1550–1554.
- King, R. B., Kapour, P. N. & Kapour, R. N. (1971). *Inorg. Chem.* **10**, 1841–1850.
- Pflugrath, J. W. & Messerschmidt, A. (1989). *MADNES*. Version of 11 September 1989. Distributed by Delft Instruments, Delft, The Netherlands.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. Univ. of Göttingen, Germany.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
- Uriarte, R., Mazanec, T. J., Tau, K. D. & Meek, D. W. (1980). *Inorg. Chem.* **19**, 79–85.

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Pentacarbonyl(difluoromethyl isocyanide)-chromium at 128 K

DIETER LENTZ AND DAGMAR PREUGSCHAT

*Institut für Anorganische und Analytische Chemie,
Freie Universität Berlin, Fabeckstrasse 34-36,
D-14195 Berlin, Germany*

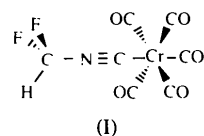
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Abstract

The monomeric molecule of the title compound, [Cr(C₂HF₂N)(CO)₅], is best described as an octahedral complex of chromium(0). The Cr—C bond distance to the difluoromethyl isocyanide ligand [1.956 (2) Å] is longer than the distances to the carbonyl ligands [Cr—CO_{cis} 1.909 (2)–1.915 (2), Cr—CO_{trans} 1.900 (2) Å], indicating a smaller π-acceptor/σ-donor ratio of the isocyanide ligand in comparison with the carbonyl ligands.

Comment

The structural data of complexes of the type (CO)₅CrL can provide important information on the properties of the ligand L, both from the Cr—L distance and from the Cr—C distance to the *trans* carbonyl ligand, which is very sensitive to the σ-donor/π-acceptor ratio of the ligand L. In order to obtain more detailed information on the fluorine-substitution effect in methyl isocyanides, the structure of pentacarbonyl(difluoromethyl isocyanide)-chromium, (I) (m.p. 300 K), was determined at 128 K.



A view of the title molecule and the atom-numbering scheme are given in Fig. 1. The Cr atom is almost octahedrally coordinated by five carbonyl ligands and the difluoromethyl isocyanide ligand. The Cr—C distances to the *cis* carbonyl ligands are similar within 2σ and close to that found for hexacarbonylchromium (Jost, Rees & Yelon, 1975; Whitaker & Jeffery, 1967), whereas this bond distance is slightly shorter for the *trans* carbonyl ligand. The Cr—C distances for related (CO)₅Cr(CNR) complexes are summarized in Table 3 and show that a short Cr—C bond to the isocyanide ligand results in a long Cr—C bond to the *trans* carbonyl ligand and *vice versa*. Short metal–carbon bonds are observed for the strong π-acceptor isocyanide ligand. Although a direct comparison with the trifluoromethyl isocyanide ligand is not possible since the electron-diffraction data for [(CO)₅Cr(CNCF₃)] (Oberhammer & Lentz, 1985) have not allowed determination of individual Cr—C bond lengths, a Cr—C bond of 1.956 (2) Å suggests that, in agreement with the spectroscopic data of Lentz & Preugschat (1992a), the difluoromethyl isocyanide moiety is the weaker π-acceptor ligand. A very short Cr—C bond of 1.814 (6) Å to the strong π-acceptor

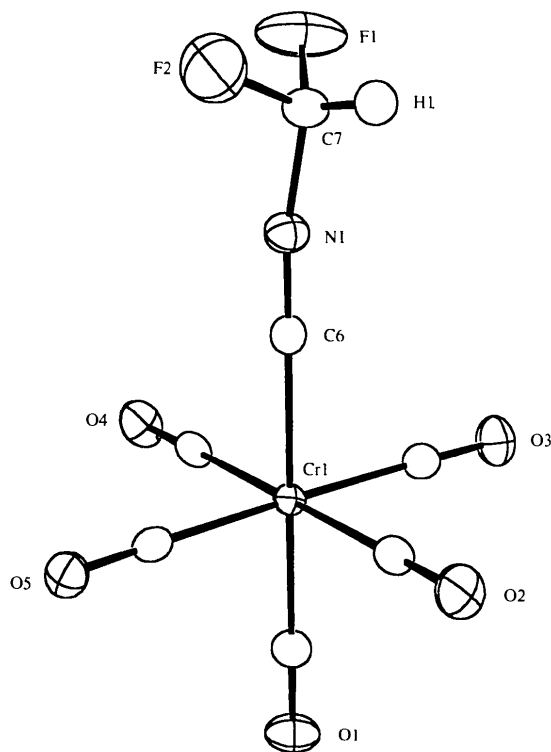


Fig. 1. Molecular structure of the title compound with the crystallographic numbering scheme (ORTEP; Johnson, 1971).

ligand $\text{CF}_3\text{—NC}$ and a long Cr—C bond of 2.017 (5) Å to the $\text{CH}_3\text{—NC}$ ligand have been found for *trans*-(CO)₄ $\text{Cr}(\text{CNCF}_3)(\text{CNCH}_3)$ (Lentz, Pötter, Marschall, Brüdgam & Fuchs, 1990), demonstrating the effects of fluorine substitution on these isocyanide ligands.

Experimental

Crystals of the title complex were prepared from (CO)₅ $\text{Cr}(\text{NCCl}_2\text{H})$ and HgF_2 (Lentz & Preugschat, 1992a), and grown by slow sublimation at room temperature and 1013 mbar (1 mbar = 100 Pa). The chosen crystal was mounted on the end of a glass fibre.

Crystal data

[$\text{Cr}(\text{C}_2\text{HF}_2\text{N})(\text{CO})_5$]
 $M_r = 269.09$
 Triclinic
 P1
 $a = 6.477(1)$ Å
 $b = 8.386(2)$ Å
 $c = 9.448(1)$ Å
 $\alpha = 82.09(2)^\circ$
 $\beta = 69.62(2)^\circ$
 $\gamma = 82.36(2)^\circ$
 $V = 474.48(14)$ Å³
 $Z = 2$
 $D_x = 1.883$ Mg m⁻³

Mo $K\alpha$ radiation
 $\lambda = 0.71069$ Å
 Cell parameters from 25 reflections
 $\theta = 17\text{--}24^\circ$
 $\mu = 1.242$ mm⁻¹
 $T = 128(5)$ K
 Platelet
 $0.7 \times 0.7 \times 0.1$ mm
 Colourless

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	x	y	z	U_{eq}
Cr1	0.16719 (4)	0.18414 (3)	0.22070 (3)	0.01277 (13)
C1	0.0496 (3)	0.4008 (2)	0.1891 (2)	0.0192 (3)
O1	-0.0259 (3)	0.5299 (2)	0.1744 (2)	0.0308 (4)
C2	0.4630 (3)	0.2436 (2)	0.1245 (2)	0.0200 (3)
O2	0.6379 (2)	0.2792 (2)	0.0657 (2)	0.0320 (4)
C3	0.1748 (3)	0.2317 (2)	0.4106 (2)	0.0193 (3)
O3	0.1783 (3)	0.2626 (2)	0.5226 (2)	0.0296 (3)
C4	-0.1293 (3)	0.1250 (2)	0.3149 (2)	0.0179 (3)
O4	-0.3053 (2)	0.0931 (2)	0.3709 (2)	0.0270 (3)
C5	0.1663 (3)	0.1411 (2)	0.0276 (2)	0.0170 (3)
O5	0.1700 (2)	0.1179 (2)	-0.0886 (2)	0.0231 (3)
C6	0.2792 (3)	-0.0394 (2)	0.2617 (2)	0.0163 (3)
N1	0.3406 (3)	-0.1731 (2)	0.2886 (2)	0.0219 (4)
C7	0.4483 (3)	-0.3234 (2)	0.3229 (2)	0.0223 (4)
F1	0.3208 (3)	-0.3941 (2)	0.4543 (2)	0.0563 (5)
F2	0.4713 (3)	-0.4214 (2)	0.2216 (2)	0.0584 (5)

Table 2. Selected geometric parameters (Å, °)

Cr1—C1	1.900 (2)	Cr1—C6	1.956 (2)
Cr1—C3	1.909 (2)	C6—N1	1.163 (2)
Cr1—C5	1.910 (2)	N1—C7	1.412 (2)
Cr1—C2	1.914 (2)	C7—F2	1.303 (3)
Cr1—C4	1.915 (2)	C7—F1	1.337 (2)
N1—C6—Cr1	178.30 (15)	F2—C7—N1	110.4 (2)
C6—N1—C7	169.7 (2)	F1—C7—N1	109.3 (2)
F2—C7—F1	105.6 (2)		

Table 3. Cr—C distances (Å) and C—N—C angles (°) in (CO)₅ $\text{Cr}(\text{CNR})$ complexes

	Cr—CN	Cr—CO _{trans}	Cr—CO _{cis}	C—N—C
(CO) ₅ $\text{Cr}(\text{CNCN})$ ^a	1.883 (3)	1.913 (4)	1.903 av.	168.5 (4)
<i>cis</i> -C ₄ H ₆ [NCCr(CO) ₅] ₂ ^b	1.903 (6)	1.899 (6)	1.881(7)–1.914 (6)	155.7 (5)
(CO) ₅ $\text{Cr}(\text{CN-CF}_3)$ ^c	1.900 (6)	1.895 (6)		163.8 (7)
(CO) ₅ $\text{Cr}(\text{CN-CO-C}_6\text{H}_5)$ ^d	1.918 (3)	1.918 (3)	1.918 (3)	142 (4)
(CO) ₅ $\text{Cr}(\text{CN-CF}=\text{CF}_2)$ ^e	1.928 (3)	1.899 (3)	1.890 (4)–1.908 (4)	173.9 (3)
(CO) ₅ $\text{Cr}\{\text{CN-C}[\text{Co}_3(\text{CO})_9]\}$ ^f	1.942 (2)	1.909 (2)	1.902 (2)–1.914 (2)	173.6 (2)
(CO) ₅ $\text{Cr}\{\text{CN-C}[\text{Co}_3(\text{CO})_9]\}$ ^f	1.961 (4)	1.860 (4)	1.885 (3)–1.903 (4)	176.0 (3)
(CO) ₅ $\text{Cr}\{\text{CN-CH}_2\text{-C}(\text{CH}_3)(\text{CH}_2\text{NC})_2\}$ ^g	1.988 (2)	1.882 (2)	1.901 (2)–1.909 (2)	178.2 (2)
(CO) ₅ $\text{Cr}(\text{CN-NH}_2)$ ^h	2.000 (3)	1.861 (3)	1.879 (3)–1.898 (4)	170.3 (3)
[(CO) ₅ $\text{Cr}(\text{CN-H-NC})\text{Cr}(\text{CO})_5$] ⁻ⁱ	2.012 (6)	1.847 (6)	1.894 av.	
(CO) ₅ $\text{Cr}\{\text{CN-NP}(\text{C}_6\text{H}_5)_3\}$ ^h	2.031 (1)	1.861 (3)	1.887 (3)–1.901 (3)	174.2 (2)

References: (a) Christian, Stolzenberg & Fehlhammer (1992); (b) Lentz, Nowak, Preugschat & Wasgindt (1993); (c) Oberhammer & Lentz (1985), data from electron diffraction; (d) Le Marouille & Caillet (1982); (e) Lentz & Preugschat (1992b); (f) Fehlhammer, Degel & Stolzenberg (1981); (g) Hahn & Tamm (1992); (h) Stolzenberg (1983); Fehlhammer, Stolzenberg & Weinberger, unpublished results; (i) Bär, Fuchs, Rieger, Aguilar-Parrilla, Limbach & Fehlhammer (1991).

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω -2 θ scans
 Absorption correction: ψ scan of 7 reflections
 $T_{\text{min}} = 0.7851$, $T_{\text{max}} = 0.9995$
 2768 measured reflections
 2281 independent reflections
 2130 observed reflections
 $[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0131$
 $\theta_{\text{max}} = 27.95^\circ$
 $h = 0 \rightarrow 8$
 $k = -10 \rightarrow 11$
 $l = -11 \rightarrow 12$
 3 standard reflections
 frequency: 90 min
 intensity decay: 0.1%

Refinement

Refinement on F^2
 $R(F) = 0.0334$
 $wR(F^2) = 0.1060$
 $S = 1.091$
 2277 reflections
 150 parameters
 H atoms refined isotropically
 $w = 1/[\sigma^2(F_o^2) + (0.0641P)^2 + 0.3101P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.786$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.743$ e Å⁻³
 Extinction correction: *SHELXL93* (Sheldrick, 1993)
 Extinction coefficient: 0.0095 (39)
 Atomic scattering factors from *International Tables for Crystallography* (1992), Vol. C, Tables 4.2.6.8 and 6.1.1.4)

The structure was solved by Patterson methods. The H atom was located from a difference map and refined isotropically. Non-H atoms were treated anisotropically by full-matrix least-squares techniques using all data except for four reflections (100, 110, $\bar{1}02$, 102) which were suspected of strong extinction.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1971) in the *NRCVAX* package (Gabe, Le Page, Charland, Lee & White, 1989).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1080). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Bär, E., Fuchs, J., Rieger, D., Aguilar-Parrilla, F., Limbach, H.-H. & Fehlhämmer, W. P. (1991). *Angew. Chem.* **103**, 88–90; *Angew. Chem. Int. Ed. Engl.* **30**, 88–90.
- Christian, G., Stolzenberg, H. & Fehlhämmer, W. P. (1992). *J. Chem. Soc. Chem. Commun.* pp. 184–185.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5. Enraf–Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
- Fehlhämmer, W. P., Degel, F. & Stolzenberg, H. (1981). *Angew. Chem.* **93**, 184–185; *Angew. Chem. Int. Ed. Engl.* **20**, 214–215.
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- Hahn, F. E. & Tamm, M. (1992). *Chem. Ber.* **125**, 119–121.
- Johnson, C. K. (1971). *ORTEPII*. ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
- Jost, A., Rees, B. & Yelon, W. B. (1975). *Acta Cryst.* **B31**, 2649–2658.
- Le Marouille, J. Y. & Caillet, P. (1982). *Acta Cryst.* **B38**, 267–269.
- Lentz, D., Nowak, F., Preugschat, D. & Wasgindt, M. (1993). *Angew. Chem.* **105**, 1547–1549; *Angew. Chem. Int. Ed. Engl.* **32**, 1456–1458.
- Lentz, D., Pötter, B., Marschall, R., Brüdgam, I. & Fuchs, J. (1990). *Chem. Ber.* **123**, 257–260.
- Lentz, D. & Preugschat, D. (1992a). *J. Organomet. Chem.* **436**, 185–188.
- Lentz, D. & Preugschat, D. (1992b). *J. Chem. Soc. Chem. Commun.* pp. 1523–1524.
- Oberhammer, H. & Lentz, D. (1985). *Inorg. Chem.* **24**, 1271–1273.
- Sheldrick, G. M. (1985). *SHELXS86. Crystallographic Computing 3*, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175–189. Oxford Univ. Press.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
- Stolzenberg, H. (1983). Dissertation, pp. 133–152, Univ. Erlangen-Nürnberg, Germany.
- Whitaker, A. & Jeffery, J. W. (1967). *Acta Cryst.* **23**, 977–989.

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Tris(*O,O'*-dicyclohexyl dithiophosphato-S,S')chromium(III)

REN-GEN XIONG AND XIAO-ZENG YOU

Institute and State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210008, People's Republic of China

XIAO-YING HUANG

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Academia Sinica, Fuzhou 350002, People's Republic of China

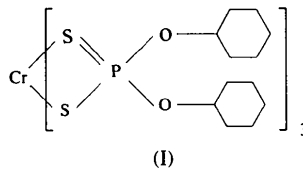
(Received 12 December 1994; accepted 5 June 1995)

Abstract

The title complex, [Cr{S₂P(OC₆H₁₁)₂}₃], contains a CrS₆ distorted octahedral core, in which the Cr—S bond lengths range from 2.423 (2) to 2.439 (2) Å and the S—Cr—S bidentate angles range from 81.39 (6) to 81.66 (7)°.

Comment

Chromium complexes such as those with dialkyl dithiophosphates and alkylphosphonic acid monoalkyl ester were found to have practical applications in the petroleum and plastics industries (Xiong & Dong, 1994a,b; Mikhailov, Kokhanov, Kazaryan, Matveeva & Kozodoi, 1972). We report here the crystal structure of the title complex, (I), which is very similar to that of [Cr{S₂P(OC₂H₅)₂}₃] (Schousboe-Jensen & Hazell, 1972).



The crystal structure of [Cr{S₂P(OC₆H₁₁)₂}₃] is composed of four neutral molecules per unit cell in the *P2₁/n* space group. The central Cr atom has distorted octahedral coordination with six S atoms from three dithiophosphate bidentate ligands. The Cr—S bond lengths [2.423 (2)–2.439 (2) Å] and S—Cr—S bidentate bond angles [81.39 (6)–81.66 (7)°] do not differ significantly from those of [Cr{Sr₂P(OC₂H₅)₂}₃] [2.421 (3)–2.430 (3) Å and 82.5 (1)°, respectively (Schousboe-Jensen & Hazell, 1972)].