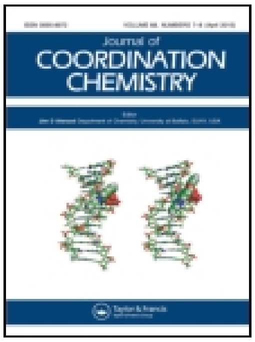

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# Crystal structures of chloro-, bromo-, and nitro-substituted chromium(III) acetylacetonates

IRINA V. SVISTUNOVA†*, MICHAIL A. PUSHILIN‡ and NATALIA A. GELFAND†

†School of Natural Sciences, Far Eastern Federal University, Vladivostok, Russian Federation
‡Laboratory of X-ray Analysis, Institute of Chemistry, FEB RUS, Vladivostok, Russian Federation

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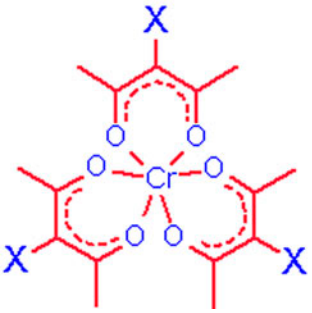

The molecular and crystal structures of chlorine-, bromine-, and nitro-substituted chromium(III) acetylacetonate are determined. Connecting the substituent to the central atom does not change bond lengths and valence angles in metal chelate rings. Studied chromium complexes are characterized by greater intermolecular interactions compared with analogous metal acetylacetonates. In some cases, intermolecular interactions increase the bend of chelate rings along the O···O line. Substituents do not interact with chromium ions of neighboring molecules because metal is blocked by three ligands.

*Keywords*: β-Diketonate; Chloroacetylacetonate; Bromoacetylacetonate; Nitroacetylacetonate; Crystal structure

## 1. Introduction

Availability of acetylacetonate complexes led to expansion of their application, for example, they are effective as catalysts in bioorganic processes [1], additives enhancing polymer's dielectric permeability [2], building unit of tunable electronic and optical materials and as an external chemical exciter [3]. Prediction of useful features is impossible without collection and systematization of structural data obtained by various methods such as X-ray

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*Corresponding author. Email: svistunova.iv@dvfu.ru structure analysis, electron diffraction analysis (GED), quantum chemical calculations, etc. These make possible verification and improvement of existing theories of chemical bonding [4] and acquisition of new models. For example, structural data were used to calculate thermodynamic characteristics [5]. Possibility of acetylacetonate application is connected with the presence of different functional groups in its structure. The concept of metal β-diketonates as quasiaromatic compounds aroused interest in synthesis of their derivatives via electrophilic substitution [6]. Subsequently, other methods of synthesis of metalochelates, containing substituents near central carbon (γ), were proposed. The greatest interest was attracted by octahedral complexes of trivalent metals, where ligands block the metal ion, making these complexes very similar to ordinary organic compounds.

The electronic spectra study of substituted acetylacetonates showed that all of the substituents on γ-carbon can be divided into two groups [7, 8]. Linkage to the chelate ring halogens and some sulfur-containing groups causes bathochromic shift of all adsorption maxima, ascribed to increase in conjunction chain between the π-system of chelate rings and substituent's p-electrons. Insertion of nitro, thiocyanate, or acyl groups into the molecule raises the energy of electronic transitions (hypsochromic shift), caused by impossibility of conjunction between substituent's p-electrons, possessing no spherical symmetry, and π-electron system of the chelate ring because of steric obstacles arising from β-methyl groups.

We were interested in the way substituents of different types influence the structure of tris-chelates. To answer this question, we examined the structures of chloro-, bromo-, and nitro-substituted chromium acetylacetonates. $Cr(acacCl)_3$ (**1**) and $Cr(acacBr)_3$ (**2**) contain substituents of the first type, while there is a substituent of the second type in $Cr(acacNO_2)_3$ (**3**).

Currently, information concerning the structure of metal β-diketonates is very limited. The structure of $Ru(acacBr)_3$ was identified [9]. Three halogen-substituted iridium acetylacetonates were described [10, 11]. Recently, a communication about $Co(acacNO_2)_3$ [12] has appeared. There are data reported in the literature about structures of substituted bis-acetylacetonates, for example, $Cu(acacCl)_2$ [13], $Cu(acacNO_2)_2$ [14], not fully substituted chelates $((Hacac)_2Ru(acacS))_2$ [15], $Co(acac)_2(acacNO_2)$ [16], and complexes, containing not only diketonate ligands $((MeO)Cr(acacBr)_2)_2$ [17].

## 2. Experimental

Synthesis of chelate **1**: to the cooled (−10 to −8) °C solution of 2.00 g $Cr(acacH)_3$ (5.73 mmol) in 50 mL of chloroform (dried) during 5 min under stirring was added dropwise solution of 2.52 g $SO_2Cl_2$ (18.67 mmol) in 10 mL of chloroform. After 20-min reaction mixture was flushed three times with water and dried under $MgSO_4$. After solvent removal, precipitate was recrystallized from benzene–petroleum ether blend (1 : 3), yield 62%. Exploitation of this blend was carried out with special care because of the carcinogenic character of benzene. Purity was controlled via thin-layer chromatography: «Sorbfil UF», eluent – benzene, detection method – UV 254 nm. Obtained product does not have traces of unsubstituted complexes, $R_f(Cr(acacCl)_3) = 0.58$. Large crystals were obtained under slow crystallization from petroleum ether–benzene. By element analysis, crystals have higher carbon content due to trapping of benzene molecules. C(found) = 42.14%, calculated for $Cr(acacCl)_3 \cdots 0.25(C_6H_6)$: 41.97%.

Chelates **2** and **3** were obtained via standard methods [18, 19].

Complex **2** was four times recrystallized from benzene–petroleum ether blend (90–110) (1 : 1) to remove traces of unsubstituted chelate (Cr(acacH)(acacBr)$_2$). Purity was controlled via thin-layer chromatography under the described conditions: R$_f$(Cr(acacBr)$_3$) = 0.59, R$_f$(Cr(acacH)(acacBr)$_2$) = 0.28. Large crystals were obtained by slow crystallization under described conditions. Melting point = 227–229 °C, from the literature: 228–229 °C [18]. C(found), % = 30.61%, calculated for Cr(acacBr)$_3$: 30.74%.

Complex **3** was three times recrystallized from chloroform–alcohol (1 : 2). R$_f$(Cr (acacNO$_2$)$_3$ = 0.61 (benzene–acetone, 15 : 0.5). Large crystals were obtained by slow crystallization under described conditions. Melting point = 253–256 °C, from the literature: 256–257 °C [19]. C(found), % = 37.33%, calculated for Cr(acacNO$_2$)$_3$: 37.20%.

X-ray experiments for **1** and **2** were performed on a KAPPA APEXII CCD diffractometer from single crystals of prismatic shape (Mo$K_\alpha$ radiation, graphite monochromator). The data were collected via combination of $\varphi$- and $\omega$-scan over a hemisphere of reciprocal space; the crystal-to-detector distance was 45 mm. X-ray absorption in the sample was taken into account by equivalent reflections (by the single crystal face indices).

The X-ray experiment for **3** was performed on a SMART APEXII CCD diffractometer (Mo$K_\alpha$ radiation, graphite monochromator). The data were collected via combination of $\omega$-scans over a whole sphere of reciprocal space; the crystal-to-detector distance was 50 mm. X-ray absorption in the sample was taken into account by equivalent reflections (by the single crystal face indices).

The structure was solved by the direct method and refined by the least-squares technique in the anisotropic approximation for non-hydrogen atoms. Sites of hydrogens were calculated geometrically and included in the refinement using the riding model.

The data were collected and edited and the unit cell parameters were refined using APEX [20]. All calculations related to the structure solution and refinement were performed using the SHELXTL/PC software [21].

Crystal chemical information on the structure investigated was deposited with the Cambridge Structural Database under number CCDC 995565, 995564, and 995566, from where it can be obtained free on request at the following website: www.ccdc.cam.ac.uk/products/csd/faqs. Main crystallographic data and the results of structure refinement are listed in table 1; bond lengths and angles are given in Supplemental data. The structure of **1–3**, numeration of atoms, and chelate rings are shown in figures 1–3.

## 3. Results and discussion

Structures of **1–3** are very similar to the structure of unsubstituted Cr(acacH)$_3$: all complexes are isolated molecules with slightly distorted octahedral environment of chromium ion. Chelate rings of single complex are not equivalent – they differ from each other by bond lengths and valence angles. That is why it is very convenient to use mean magnitudes, presented in table 2. In spite of quasiaromatic concept of acetylacetonate complexes, chelate cycles in **1–3** are not flat, they bend along O···O and C$_\beta$···C$_\beta$. Earlier, the bend in chelate metallocycles was reported [10, 22].

Substituents change a little the bond lengths and valence angles in chelate cycles. O–C$_\beta$ and C$_\beta$–C$_\gamma$ bond lengths increased insignificantly (0.01 Å) in all three complexes (table 2). Cr–O bond lengths stay virtually unchanged, while intraligand distance O···O reduced by 0.04 Å. Indicated reduction caused by decrease in intraligand angle O–Cr–O approximately

Table 1. Crystallographic data, parameters of the diffraction experiments, and structure refinement.

| Parameter | Value | | |
|---|---|---|---|
| | **1** | **2** | **3** |
| Formula | $C_{15}H_{18}Cl_3CrO_6 \times 0.25\ C_6H_6$ | $C_{15}H_{18}Br_3CrO_6$ | $C_{15}H_{18}N_3CrO_{12}$ |
| Temperature, K | 472.17 | 586.02 | 484.32 |
| Molecular weight | 170(1) K | 170(1) K | 170(1) K |
| Wavelength, Å | | Mo$K_\alpha$ (0.71073 Å) | |
| Syngony | Monoclinic | Monoclinic | Tetragonal |
| Space group | $P2_1/c$ | $P2_1/n$ | $I4_1/cd$ |
| Unit cell parameters, Å, deg. | $a = 7.8919(1)$<br>$b = 18.2013(2)$<br>$c = 28.1702(4)$<br>$\beta = 95.450(1)$ | $a = 12.7689(6)$<br>$b = 9.9271(4)$<br>$c = 15.7064(8)$<br>$\beta = 105.822(1)$ | $a = 32.9692(6)$<br>$c = 7.5146(2)$ |
| $V$, Å$^3$ | 402,816(9) | 19,155(2) | 81,681(4) |
| $Z$ | 8 | 4 | 16 |
| $d_{выч.}$ (g cm$^{-3}$) | 1.557 | 2.032 | 1.575 |
| $\mu$, mm$^{-1}$ | 0.995 | 6.883 | 0.629 |
| $F(0\ 0\ 0)$ | 1932 | 1140 | 3984 |
| Crystal size, mm | 0.42 × 0.25 × 0.16 | 0.44 × 0.32 × 0.18 | 0.33 × 0.31 × 0.28 |
| Range of data collection over $q$, deg. | 1.33–31.54 | 1.83–32.06 | 0.873–30.544 |
| Intervals of reflection indices | $-11 \le h \le 11$, $-26 \le k \le 26$,<br>$-41 \le l \le 41$ | $-19 \le h \le 19$,<br>$-14 \le k \le 14$,<br>$-23 \le l \le 23$ | $-47 \le h \le 47$,<br>$-47 \le k \le 47$,<br>$-10 \le l \le 10$ |
| Number of means./indep. reflections | 66,701 | 33,463 | 89,730 |
| Completeness over $q = 28.02$, % | 13,445 ($R_{int} = 0.0219$) | 6667 ($R_{int} = 0.0244$) | 6253 ($R_{int} = 0.0194$) |
| Number of reflections with $I > 2s(I)$ | 11,251 | 5584 | 6069 |
| Refinement method | | Total matrix OLS on $F^2$ | |
| Number of refined variables | 572 | 233 | 317 |
| GooF | 1.031 | 1.032 | 1.062 |
| $R$-factors over $F^2 > 2s(F^2)$ | $R1 = 0.0335$<br>$wR2 = 0.0836$ | $R1 = 0.0250$<br>$wR2 = 0.0515$ | $R1 = 0.0296$<br>$wR2 = 0.0828$ |
| $R$-factors over all reflections | $R1 = 0.0433$<br>$wR2 = 0.0889$ | $R1 = 0.0361$<br>$wR2 = 0.0553$ | $R1 = 0.0307$<br>$wR2 = 0.0838$ |
| Extinction coefficient | Not refined | 0.00262(8) | Not refined |
| Flack's parameter | | | 0.014(3) |
| Residual electron density (min/max) (e Å$^{-3}$) | −0.932/1.228 | −0.926/0.841 | −0.277/0.430 |

by 1° and, most probably, caused by alteration of angles inside chelate cycle due to increase in sterical repulsion between γ-substituent and β-methyl groups within the substitution of hydrogen atom by Cl-, Br-, and $NO_2$-group.

Thus, substituents with different influences on electronic system of chelate cycles have equal impact on their structure.

$Cr(acacCl)_3$ crystallizes through two crystallographically independent molecules, which differs by bond lengths, valence angles, and bend of the cycles. Similar packing was identified for $Ir(acacCl)_3$ [5]. Molecules, forming the crystallographic pair, are optical isomers. Mean magnitudes of corresponding bond lengths in paired molecules are equal – table 2. Bend of chelate cycles is the most significant difference between the molecules. Bending is considerably higher in the molecule, consisting of A–B–C cycles, compared to unsubstituted chelate. The highest bend angle is observed in A cycle along the O···O line – 11.4°, while

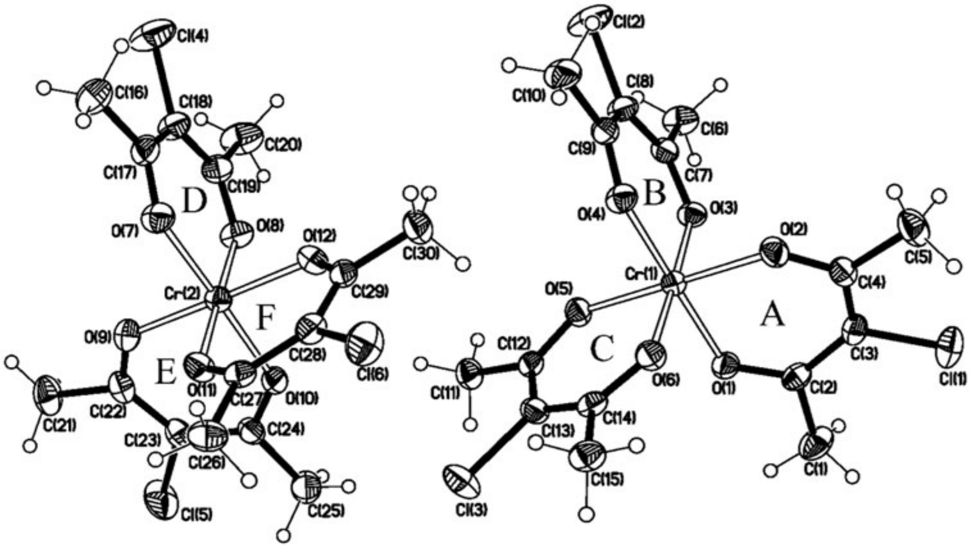

Figure 1. Molecular structure, enumeration of atoms, and cycles in Cr(acacCl)$_3$ (**1**) (shown without coordinated benzene molecules).

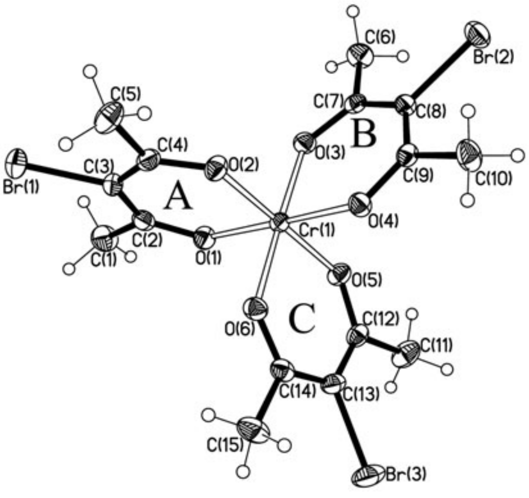

Figure 2. Molecular structure, enumeration of atoms, and cycles in Cr(acacBr)$_3$ (**2**).

mean magnitude (A–B–C) – 7.8° (table 2). In the second molecule in pair – all chelate cycles are flat. One can propose that the bend of a single cycle is caused by intermolecular interactions: Cr(acacCl)$_3$ crystallizes such that two of three chlorines are in contact with chlorines of neighboring molecules, forming endless chains: Cr(acacCl···Clacac)Cr(acacCl)(acacCl···Clacac)Cr. Only molecules with identical crystallographic characteristics and same optical isomers are included into one chain. Paired molecules form a second chain – figure 4.

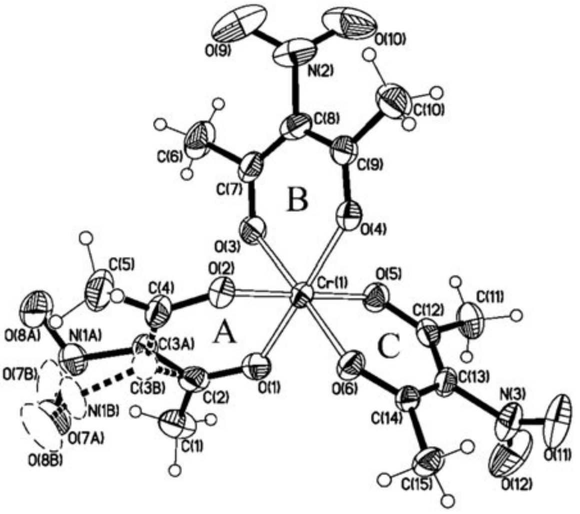

Figure 3. Molecular structure, enumeration of atoms, and cycles in $Cr(acacNO_2)_3$ (**3**).

Table 2. Mean geometric characteristics of **1–3** and some acetylacetonates of Co(III), Ir(III), and Ru(III)[a].

| | Bond length, Å | | | | | | | Bending of cycle along | |
|---|---|---|---|---|---|---|---|---|---|
| | M–O | C–O | $C_\beta$–$C_\gamma$ | $C_\beta$–Me | C–X | N–O | Intraligand distance (O···O), Å | Line O···O, deg. | Line $C_\beta$···$C_\beta$, deg. |
| $Cr(acacH)_3$ [24] | 1.95 | 1.26 | 1.39 | 1.52 | | | 2.79 | 4.89 | 2.99 |
| $Cr(acacCl)_3$ (ABC) | 1.95 | 1.27 | 1.40 | 1.50 | 1.75 | | 2.75 | 7.75 | 4.46 |
| $Cr(acacCl)_3$ (DEF) | 1.95 | 1.27 | 1.40 | 1.50 | 1.75 | | 2.76 | 1.73 | 0.91 |
| $Cr(acacCl)_3$[b] | 1.95 | 1.27 | 1.40 | 1.50 | 1.75 | | 2.75 | 8.13 | 5.26 |
| $Cr(acacBr)_3$ | 1.95 | 1.28 | 1.41 | 1.50 | 1.91 | | 2.75 | 3.85 | 1.03 |
| $Cr(acacNO_2)_3$ | 1.94 | 1.26 | 1.41 | 1.50 | 1.45 | 1.22 | 2.73 | 7.88 | 5.73 |
| $Co(acacH)_3$ [25] | 1.88 | 1.27 | 1.39 | 1.51 | | | 2.81 | 4.74 | 2.32 |
| $Co(acacNO_2)_3$ [12] | 1.87 | 1.26 | 1.40 | 1.50 | 1.46 | 1.22 | 2.76 | | |
| $Ir(acacH)_3$ [23] | 2.02 | 1.27 | 1.40 | 1.50 | | | 2.97 | 2.50 | 3.16 |
| $Ir(acacCl)_3$ (ABC) [10] | 2.01 | 1.28 | 1.37 | 1.56 | 1.78 | | 2.94 | 7.05 | 4.36 |
| $Ir(acacCl)_3$ (DEF) [10] | 1.99 | 1.29 | 1.41 | 1.57 | 1.76 | | 2.91 | 1.41 | 6.04 |
| $Ir(acacCl)_3$[b] [10] | 2.00 | 1.28 | 1.39 | 1.56 | 1.77 | | 2.92 | 4.23 | 5.20 |
| $Ir(acacBr)_3$ [11] | 1.99 | 1.29 | 1.37 | 1.51 | 1.93 | | 2.90 | 2.04 | 3.62 |
| $Ru(acacH)_3$ [9] | 2.00 | 1.27 | 1.38 | 1.49 | | | 2.90 | 2.60 | 1.88 |
| $Ru(acacBr)_3$ [9] | 2.00 | 1.28 | 1.40 | 1.50 | 1.91 | | 2.85 | 3.06 | 1.34 |

[a] Geometric values for complexes of cobalt, iridium, and ruthenium are obtained from cited works.
[b] Mean for two molecules.

The highest bending of cycles possesses moieties with the lowest Cl···Cl distance (3.343 Å) and linear Cl···Cl lies in plane normal to the chelate cycle, leading to bending of the cycle along O···O and $C_\beta$···$C_\beta$ in the opposite direction.

Such peculiarities are also present in $Ir(acacCl)_3$, investigated earlier [5]. Two molecules, forming a crystallographic pair, match each other by mean bond length and differ by bending angle of chelate rings: there are highly bended in one molecule, while flat in the other.

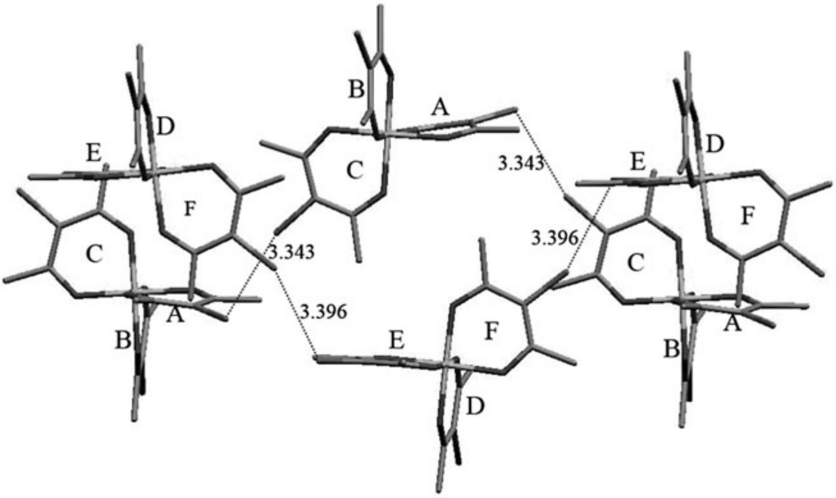

Figure 4. Chain formation from crystallographically identical molecules via interaction between chlorines.

Chelate cycle bending, as for **1**, is caused by interaction of chlorines of neighboring molecules. Interaction occurs between molecules with identical crystallographic characteristics. However, unlike the chromium complex, only two molecules interact in Ir(acacCl)$_3$ rather than a chain.

The most significant difference in structure of **1** and iridium [5] chloroacetylacetonate is C–C bond length in β-methyl groups. C–C bond length of 12 methyl groups in two crystallographically independent molecules significantly differs (by 0.152 Å), reaching 1.631 Å, considerably higher than unsubstituted chelate (1.502 Å [23], mean magnitude). Incorporating chlorine into chromium acetylacetonate slightly reduces (0.02 Å) C–C bond length, while this bond length slightly changes from one methyl group to another (not more than 0.01 Å).

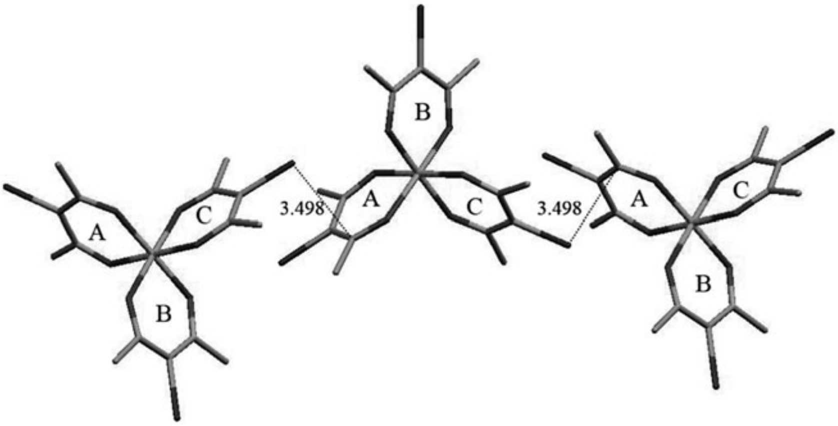

Figure 5. Intermolecular interactions in **2**.

Primary crystallographic unit of Cr(acacBr)$_3$ is one molecule. C$_\gamma$–Br bond length is 1.91 Å that corresponds to the same bond in ((RO)Cr(acacBr)$_2$)$_2$ [17], Ru(acacBr)$_3$ [9], and a bit lower than in Ir(acacBr)$_3$ (1.93 Å) [11]. The same length is observed for C–Br in aromatic compounds. Bending of chelate rings in **2** is lower than in unsubstituted chelate rings that are nearly flat. Molecules crystallize such that bromine of one molecule coordinates to the β-carbon of a neighboring molecule – figure 5. Br···C$_\beta$ distance (3.498 Å) is slightly shorter than sum of van der Waals radii of elements (3.55 Å). Interacting cycles (A and C cycles of neighboring molecules) are arranged nearly parallel. Thus, Cr(acacBr)$_3$ are built up into endless chains. Neighboring chains are optical isomers. The chelate ring from which bromine takes part in the interaction (C cycle) is bent most, and cycle is bended aside the A cycle, with which the interaction takes place. One can propose that it is caused by electrostatic interaction between bromine (in C cycle) and β-carbon of cycle A.

Primary packing of **2** consists of four molecules. Ru(acacBr)$_3$ molecules are packed similarly; however, intermolecular interactions in ruthenium complex are limited to the contacts of bromine and oxygen with hydrogen of methyl groups of neighboring molecules [9]. Ir (acacBr)$_3$ crystallizes differently with the primary unit consisting of six molecules and no short contacts [11].

One reason for more short contacts in chromium complexes compared to ruthenium and iridium chelates is the larger size of analogous chromium complexes. For estimation of molecule size, we used mean intramolecular distances from central metal to bromine, 5.21 Å (Cr···Br) – 5.19 Å (Ru···Br) – 5.16 Å (Ir···Br).

Structure and packing of **3** is as described [12] for Co(acacNO$_2$)$_3$.

As expected, nitro-group is over the ring plane because of steric influence from β-methyl groups. The rotation angle is 50–59°, lower than in aromatic analogs: in benzene derivatives, where nitro-group is surrounded by methyl groups, rotation angle is 66–86° [26–28]. Mean bond length C$_\gamma$–N in **3** is 1.45 Å that matches the value for the cobalt complex (1.46 Å, mean value [12]) and lower than in aromatic compounds (1.47–1.49 Å).

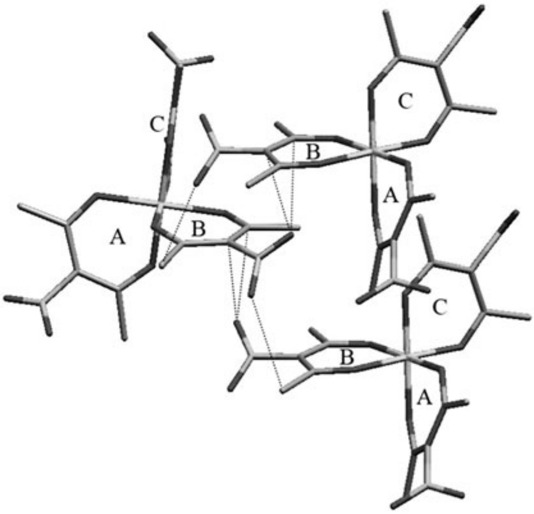

Figure 6. Intermolecular interactions in **3** through nitro-groups.

Crystal unit of **3**, as for Co(acac$NO_2$)$_3$, consists of 12 molecules. Analysis of short contacts shows that molecules connected through interactions like C–H···O, occurring between hydrogens of methyl groups, carbonyl oxygens of cycle B, and oxygens of all three nitro-groups (figure 6).

One oxygen of nitro, connected with cycle B, interacts with $C_\beta$–$C_\gamma$ bond of cycle B of a neighboring molecule, whose nitro interacts with the next molecule, similar to packed molecules of Co(acac$NO_2$)$_3$ [12]. Unlike Cu(acac$NO_2$)$_2$ [14], there is no interaction between nitro and metal ion of neighboring molecules in **3** due to isolation of chromium ion coordination sphere in acetylacetonate complexes.

Thus, implementing γ-substituent does not change the molecular structure of chromium acetylacetonate. Therefore, substituents that differently render the electronic system of the complex affect the molecular structure of tris-chelate identically. Molecular structure of substituted chromium acetylacetonates mainly repeats the structures of similar benzene derivatives, in which two methyl groups are situated near the substituent. Coordination nature of the radical does not affect significantly the structure and packing of substituted derivatives of chromium acetylacetonate. Specific difference of studied compounds from aromatic analogs is the non-planar structure of chelate cycles, their ability to bend (especially along the intraligand O···O line) under intermolecular interactions. Comparison of substituted chromium acetylacetonates with substituted acetylacetonates of heavier elements (ruthenium and iridium) shows peculiarity of chromium complexes with considerably more intermolecular interactions. Possible reason of such behavior is bigger size of chromium chelates.

## Disclosure statement

No potential conflict of interest was reported by the authors.

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## Supplemental data

Supplemental data for this article can be accessed here [http://dx.doi.org/10.1080/00958972.2015.1068302].

## References

[1] P. Zhang, C. Wang, Z. Chen, H. Li. *Catal. Sci. Technol.*, **1**, 1133 (2011).
[2] M. Lai, S. Yu, R. Sun, X. Zeng, S. Luo, C.-P. Wong. *Compos. Sci. Technol.*, **89**, 127 (2013).
[3] H. Maeda, M. Takayama, K. Kobayashi, H. Shinmori. *Org. Biomol. Chem.*, **8**, 4308 (2010).
[4] N.V. Tverdova, G.V. Girichev, S. Samdal. *Struct. Chem.*, **24**, 891 (2013).
[5] M.A. Bespyatov, V.N. Naumov. *J. Chem. Eng. Data*, **55**, 46 (2010).
[6] J.P. Collman. *Angew. Chem.*, **77**, 154 (1965).
[7] P.R. Singh, R. Sahai. *Aust. J. Chem.*, **22**, 1169 (1969).
[8] G.M. Svistunov, N.P. Shapkin. *Zh. Obshch. Khim.*, **63**, 260 (1993).
[9] T.S. Knowles, B.J. Howlin, J.R. Jones, D.C. Povey, C.A. Amodio. *Polyhedron*, **12**, 2921 (1993).
[10] V.G. Isakova, I.A. Baidina, N.B. Morozova, I.K. Igumenov, V.B. Rybakov. *J. Struct. Chem.*, **40**, 379 (1999).
[11] V.G. Isakova, I.A. Baidina, N.B. Morozova, I.K. Igumenov, V.B. Rybakov. *J. Struct. Chem.*, **40**, 331 (1999).

[12] D.H. Johnston, J.T. Brangham, C.D. Rapp. *Acta Crystallogr., Sect. E: Struct. Rep. Online*, **68**, m312 (2012).
[13] S. Sans-Lenain, A. Gleizes. *Inorg. Chim. Acta*, **211**, 67 (1993).
[14] C. Tsiamis, A.C. Stergiou, V. Anesti, N.M. Blaton, O.M. Peeters. *Inorg. Chim. Acta*, **269**, 332 (1998).
[15] A. Endo, M. Sibasaki, H. Nagao, K. Shimizu. *Inorg. Chim. Acta*, **357**, 3443 (2004).
[16] T.G. Appleton, L.R. Gahan, P.J. Oliver. *Aust. J. Chem.*, **45**, 797 (1992).
[17] E.D. Estes, R.P. Scaringe, W.E. Hatfield, D.J. Hodgson. *Inorg. Chem.*, **16**, 1605 (1977).
[18] J.P. Collman, R.A. Moss, H. Maltz, C.C. Heindel. *J. Am. Chem. Soc.*, **83**, 531 (1961).
[19] J.P. Collman, R.L. Marshall, W.L. Young, S.D. Goldby. *Inorg. Chem.*, **1**, 704 (1962).
[20] Bruker. *APEX2*, Bruker AXS Inc., Madison, Wisconsin, USA (2005).
[21] G.M. Sheldrick. *Acta Crystallogr., Sect. A: Found. Crystallogr.*, **64**, 112 (2008).
[22] L.M. Shkolnikova, M.A. Porai-Koshits. *S. Cryst. Chem. – M.: VINITI*, **16**, 117 (1982).
[23] V.G. Isakova, I.A. Baidina, N.B. Morozova, I.K. Igumenov. *Polyhedron*, **19**, 1097 (2000).
[24] S.Z. Haider, K.M.A. Malik, A. Hashem, M.B. Hursthouse. *Dhaka Univ. Stud., Part B.*, **30**, 145 (1982).
[25] L.S. Chrzanowski, M. Lutz, A.L. Spek. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, **63**, m283 (2007).
[26] Y.B. Gatilov, N.G. Bokii, Y.T. Struchkov. *J. Struct. Chem.*, **16**, 702 (1975).
[27] J. Trotter. *Acta Crystallogr.*, **12**, 605 (1959).
[28] A. Anthony, G.R. Desiraju, R.K.R. Jetti, S.S. Kuduva, N.N.L. Madhavi, A. Nangia, R. Thaimatam, V.R. Thalladi. *Cryst. Eng.*, **1**, 18 (1998).