Reviews

The strength and length of donor-acceptor bonds in molecular complexes

I. P. Romm,[a]★ Yu. G. Noskov,[b] and A. A. Malkov[a]

[a]L. Ya. Karpov Research Physicochemical Institute,
10 ul. Vorontsovo Pole, Moscow 105064, Russian Federation.
Fax: +7 (495) 975 2450. E-mail: malkov_aa@rambler.ru
[b]Joint Research and Development Center,
55/1, Bldg. 2, Leninskiy Prosp., Moscow 119333, Russian Federation.
Tel.: +7 (495) 730 6101. E-mail: NoskovYG@yrd.ru

Numerous published data on the structure and thermodynamics of formation of molecular complexes are analyzed. The enthalpies of complexation ($-\Delta H$) are related to the characteristic parameter $\Delta r = [r_{DA} - a_1(r_D + r_A)]$, where r_{DA} is the donor-acceptor bond length determined by microwave spectroscopy and X-ray analysis, r_D and r_A are the tabulated values of the homopolar covalent radii of the heteroatoms that form the donor-acceptor bond, and a_1 is an empirical coefficient equal to 0.901±0.007. The relation between $-\Delta H$ and Δr values has the form $-\Delta H = a_2/\Delta r$ (a_2 = 21.6±1.6 kJ Å mol^{-1}), with a mean relative error of approximation of about 15% and a correlation coefficient of 0.97. As the strength of the complex increases, the donor-acceptor bond length approaches the sum of the heteropolar covalent radii of the atoms involved in the bond (Δr tends to zero). At $\Delta r \gg 1$, the strength of complexes is determined by weak van der Waals interactions between the complex components and the $-\Delta H$ values tend to zero.

Key words: molecular complex, enthalpy of formation, donor-acceptor bond, bond length.

One of the most important characteristics of molecular complexes is the enthalpy of formation ($-\Delta H$), a measure of the strength of the donor-acceptor bond. Unlike the $-\Delta H$ values for covalent bonds, the energies of formation of intermolecular donor-acceptor bonds ($-\Delta H_{DA}$/kJ mol^{-1}) vary over a rather wide range from a few to a hundred and more kJ mol^{-1}.

Numerous attempts to relate the $-\Delta H$ parameter to other characteristics of molecular complexes, *e.g.*, positions of the charge-transfer bands in electronic absorption spectra (EAS), dipole moments of complexes, changes in entropy of complexation, and the chemical shift of coor-

* Dedicated to the memory of E. N. Guryanova (1911—2004), a prominent scientist who formulated the basic principles elaborated by her disciples in this review.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 1869—1878, October, 2007.
1066-5285/07/5610-1935

dination[1,2] were made in order to understand the nature of the donor-acceptor interaction. Often, these relations are linear, as in the case of the complexes of I_2, $SnCl_4$, and $TiCl_4$ with n-donors:

$$-\Delta H_{DA} = 35.3\mu_{DA}/er_{DA}, \quad (1)$$

where μ_{DA}/er_{DA} is the degree of charge transfer from the donor (D) to acceptor (A), μ_{DA} is the dipole moment, r_{DA} is the donor-acceptor bond length, and e is the charge of electron.[1]

For these systems, there is also a linear correlation between the changes in the enthalpies and entropies ($-\Delta S$) of the complexation reactions[1]

$$-\Delta H = -0.337\Delta S + 3.1. \quad (2)$$

Analysis of the ^{19}F chemical shifts in the NMR spectra of *p*-fluorobenzophenone complexes with acceptors made it possible to establish a correlation between the enthalpies of formation of the complexes and the coordination-induced chemical shift (Δ_c) of ^{19}F nuclei, *i.e.*, the ^{19}F chemical shift differences between the complexes and free n-donors[3]

$$-\Delta H = \Delta_c[\sigma^0/2.75] + 0.7, \quad (3)$$

where σ^0 is the Hammett constant of the substituent X in the benzophenones *p*-F—C_6H_4—CO—C_6H_4—X.

An interrelation between the enthalpy of formation of a complex and the length of the donor-acceptor bond (r_{DA}) in it was hypothesized long ago.[1,4,5] Although reliable experimental data were scarce at that time, such a correlation was constructed using nonlinear functions. In this work, based on the experimental data accumulated to date, we attempted to establish a correlation between the enthalpies of complexation and the donor-acceptor bond lengths, to determine its quantitative characteristics, and to elucidate its physical meaning.

We restricted our analysis to those experimental $-\Delta H$ and r_{DA} values that are not affected by additional interactions (intermolecular hydrogen bonds, solvation effects, *etc.*). Since the donor-acceptor bond lengths determined by different methods (see below) differ appreciably, the results of gas-phase electron diffraction (GED) measurements were not included in the primary data set (Table 1); they are considered separately (Table 2).

The enthalpies of complexation listed in Tables 1 and 2 were determined from vapor pressure measurements under gas-phase dissociation (GD) of the complexes, as well as calorimetrically in the gas phase (CM, g.p.) or in solution (CM, solvent), and by electronic spectroscopy (ES), dielectrometry (DEM), and NMR spectroscopy. Among the data of solution measurements, we used only the results obtained using inert solvents including hexane,

Table 1. Donor-acceptor bond lengths (r_{DA}) determined by X-ray analysis and microwave spectroscopy (MWS), parameters $\Delta r = r_{DA} - 0.901(r_D + r_A)$,[a] and the enthalpies of formation of molecular complexes ($-\Delta H$/kJ mol^{-1})

Run	Complex	r_{DA}/Å (method)	Δr/Å	$-\Delta H$ (method)
1	$Me_3N \cdot BH_3$	1.609 (MWS)[6]	0.187	132 (CM, gas phase)[7]
2	$C_5H_5N \cdot BH_3$	1.610 (MWS)[8]	0.188	121 (CM, NO_2Ph)[9]
3	$Me_3N \cdot B(CH_3)_3$	1.698 (MWS)[10]	0.276	74 (GD)[11]
4	$Me_2HN \cdot B(CH_3)_3$	1.656 (X-ray analysis)[12]	0.234	81 (GD)[11]
5	$H_3P \cdot B(C_6F_5)_3$	2.046 (X-ray analysis)[13]	0.264	80 (GD)[13]
6	$Me_3N \cdot BF_3$	1.636 (MWS)[14]	0.214	111 (CM, gas phase)[7]
7	$C_5H_5N \cdot BF_3$	1.610 (MWS)[8]	0.188	104 (CM, benzene)[15]
8	$Et_3P \cdot BF_3$	2.028 (X-ray analysis)[16]	0.246	79[b] (GD)[17]
9	$Me_2SO \cdot BF_3$	1.54 (X-ray analysis)[18]	0.253	95 (CH_2Cl_2)[19]
10	$C_5H_5N \cdot BCl_3$	1.592 (X-ray analysis)[20]	0.170	129 (CM, NO_2Ph)[21]
11	$C_4H_8S \cdot BCl_3$	1.960 (X-ray analysis)[22]	0.232	80 (GD)[23]
12	$Me_3N \cdot BBr_3$	1.600 (X-ray analysis)[24]	0.178	139[c] (CM, benzene)[25]
13	$C_5H_5N \cdot BBr_3$	1.590 (X-ray analysis)[26]	0.168	151 (CM, benzene)[25]
14	$Me_3P \cdot BBr_3$	1.924 (X-ray analysis)[27]	0.142	168[d] (CM, benzene)[25]
15	$(n\text{-}C_3H_7)_3P \cdot BBr_3$	1.950 (X-ray analysis)[28]	0.168	168[d] (CM, benzene)[25]

(*to be continued*)

Table 1 (*continued*)

Run	Complex	r_{DA}/Å (method)	Δr/Å	$-\Delta H$ (method)
16	$Me_2S \cdot BBr_3$	1.934 (X-ray analysis)[22]	0.206	91 (CM, cyclo-hexane)[29]
17	$C_4H_8S \cdot BBr_3$	1.966 (X-ray analysis)[22]	0.238	98 (CM, benzene)[25]
18	$Me_2Se \cdot BBr_3$	2.065 (X-ray analysis)[22]	0.220	95[e] (CM, benzene)[30]
19	$Me_2NH \cdot AlMe_3$	2.000 (X-ray analysis)[31]	0.236	129 (CM, hexane)[32]
20	$Ph_3PO \cdot AlCl_3$	1.733 (X-ray analysis)[33]	0.104	211 (CM, benzene)[34]
21	$Cl_3PO \cdot AlCl_3$	1.780 (X-ray analysis)[35]	0.151	120 (GD)[36]
22	$Ph_3PO \cdot AlBr_3$	1.736 (X-ray analysis)[33]	0.107	191 (CM, benzene)[34]
23	$2MeCN \cdot SnCl_4$	2.331 (X-ray analysis)[37]	0.612	30 (CM, benzene)[38]
24	$2Et_2O \cdot SnCl_4$	2.191 (X-ray analysis)[39]	0.355	47 (CM, DCE)[40]
25	$[Me_2N]_3PO \cdot Me_3SnCl$	2.28 (X-ray analysis)[41]	0.543	42 (CM, CCl_4)[42]
26	$Ph_3PO \cdot Ph_3SnCl$	2.391 (X-ray analysis)[43]	0.654	35 (CM, benzene)[44]
27	$2C_5H_5N \cdot Me_2SnCl_2$	2.39 (X-ray analysis)[45]	0.518	37 (CM, benzene)[46]
28	$2C_5H_5NO \cdot Me_2SnCl_2$	2.25 (X-ray analysis)[47]	0.513	29 (CM, benzene)[48]
29	$2[Me_2N]_3PO \cdot Me_2SnCl_2$	2.26 (X-ray analysis)[49]	0.523	35 (ЯМР, 1,1,2,2-TCE)[50]
30	$2,2'\text{-}(C_5H_4N)_2 \cdot Ph_2SnCl_2$	2.360 (X-ray analysis)[51]	0.488	41 (CM, benzene)[46]
31	$Ph_3PO \cdot Ph_2SnCl_2$	2.278 (X-ray analysis)[52]	0.541	47 (CM, benzene)[53]
32	$2,2'\text{-}(C_5H_4N)_2 \cdot SnI_4$	2.277 (X-ray analysis)[54]	0.405	49 (CM, benzene)[55]
33	$2Et_2O \cdot TiCl_4$	2.139 (X-ray analysis)[56]	0.357	64 (CM, CH_2Cl_2)[57]
34	$Cl_3PO \cdot NbCl_5$	2.16 (X-ray analysis)[58]	0.405	62 (GD)[59]
35	$2,2'\text{-}(C_5H_4N)_2 \cdot SbCl_3$	2.281 (X-ray analysis)[60]	0.427	33 (CM, DCE)[61]
36	$2Ph_3PO \cdot SbCl_3$	2.455 (X-ray analysis)[62]	0.736	18 (CM, DCE)[61]
37	$MeCN \cdot SbCl_5$	2.23 (X-ray analysis)[63]	0.466	59 (CM, DCE)[64]
38	$Cl_3PO \cdot SbCl_5$	2.18 (X-ray analysis)[58]	0.398	49 (CM, DCE)[64]
39	$Cl_2SeO \cdot SbCl_5$	2.08 (X-ray analysis)[65]	0.298	51 (CM, DCE)[64]
40	$Me_3N \cdot SO_2$	2.260 (MWS)[66]	0.694	41 (ES, gas phase)[67]
41	$[1,4\text{-}C_4H_8O_2 \cdot Cl_2]_n$	2.67 (X-ray analysis)[68]	1.185	8.8 (ES, CCl_4)[69]
42	$[1,4\text{-}C_4H_8O_2 \cdot Br_2]_n$	2.71 (X-ray analysis)[70]	1.090	8.4 (ES, CCl_4)[71]
43	$Me_3N \cdot I_2$	2.27 (X-ray analysis)[72]	0.443	51 (ES, heptane)[73]
44	$4\text{-}MeC_5H_4N \cdot I_2$	2.31 (X-ray analysis)[74]	0.483	37 (ES, heptane)[75]
45	$1,4\text{-}C_4H_8O_2 \cdot I_2$	2.81 (X-ray analysis)[76]	1.019	16 (ES, CCl_4)[77]
46	$(PhCH_2)_2S \cdot I_2$	2.78 (X-ray analysis)[78]	0.647	20 (DEM, octane)[79]
47	$1,4\text{-}C_4H_8S_2 \cdot I_2$	2.867 (X-ray analysis)[80]	0.734	26 (ES, CCl_4)[81]
48	$C_4H_6S_3 \cdot I_2$[f]	2.755 (X-ray analysis)[82]	0.712	42 (ES, $CHCl_3$)[82]
49	$C_3H_6N_2S \cdot 2I_2$	2.487 (X-ray analysis)[83]	0.444	34[g] (ES, CCl_4)[84]
50	$Ph_3PS \cdot I_2$	2.753 (X-ray analysis)[85]	0.710	31 (CM, CCl_4)[86]

(*to be continued*)

Table 1 (*continued*)

Run	Complex	r_{DA}/Å (method)	Δr/Å	$-\Delta H$ (method)
51	$[Me_2N]_3PS \cdot I_2$	2.705 (X-ray analysis)[87]	0.662	34 (ES, heptane)[88]
52	$C_4H_8Se \cdot I_2$	2.762 (X-ray analysis)[89]	0.512	46 (ES, CCl_4)[90]
53	1,4-$C_4H_8Se_2 \cdot I_2$	2.829 (X-ray analysis)[91]	0.579	29 (ES, CCl_4)[81]
54	1,4-$OC_4H_8Se \cdot I_2$	2.755 (X-ray analysis)[92]	0.505	32 (ES, CCl_4)[81]
55	$Ph_3PSe \cdot I_2$	2.803 (X-ray analysis)[85]	0.643	39 (CM, CCl_4)[86]
56	$[Me_2N]_3PSe \cdot I_2$	2.718 (X-ray analysis)[93]	0.558	54 (ES, heptane)[88]
57	1,4-$C_4H_8O_2 \cdot 2ICl$	2.57 (X-ray analysis)[78]	0.779	22[h] (CM, benzene)[94]
58	$C_5H_5N \cdot IBr$	2.26 (X-ray analysis)[95]	0.433	51 (CM, cyclohexane)[96]
59	$Ph_3PS \cdot IBr$	2.656 (X-ray analysis)[87]	0.613	48 (CM, CCl_4)[97]

[a] The r_D and r_A values are listed in Table 3.
[b] $-\Delta H$ of complex $Me_3P \cdot BF_3$.
[c] $-\Delta H$ of complex $Et_3N \cdot BBr_3$.
[d] $-\Delta H$ of complex $Bu^n{}_3P \cdot BBr_3$.
[e] $-\Delta H$ of complex $Pr^n{}_2Se \cdot BBr_3$.
[f] $C_4H_6S_3$ is 1,3-dithiacyclohexane-2-thione.
[g] $-\Delta H$ of a 1 : 1 complex with ethylene thiourea.
[h] $-\Delta H$ of the 1,4-$C_4H_8O_2 \cdot ICl$ complex.

heptane, octane, cyclohexane, or solvents that slightly affect the thermodynamics of complexation: namely, benzene, carbon tetrachloride, 1,2-dichloroethane (DCE), and in some cases methylene chloride, chloroform, 1,1,2,2-tetrachloroethane (TCE), and nitrobenzene.

Most complexes under study (see Table 1 and 2) have the D·A (1 : 1) composition and the $-\Delta H$ values correspond to reactions of the D + A = D·A type. However, some systems have more complex chemical compositions, *e.g.*, 2 : 1, as in the case of important diethyl ether complexes with tin and titanium halides $2Et_2O \cdot SnCl_4$ and $2Et_2O \cdot TiCl_4$. The $-\Delta H$ values listed in Table 1 (runs *24* and *33*, respectively) correspond to one of the two identical donor-acceptor bonds, being halved as compared to the measured enthalpies of formation of the 2 : 1 complexes. This approach was used in the analysis of other 2 : 1 complexes of tin compounds. Some difficulties arise when comparing the $-\Delta H$ values measured in solution with the results of X-ray studies of the halogen complexes (see Table 1, runs *41*, *42*, and *49*). All the three complexes have a 1 : 1 composition $D \cdot X_2$ (X is a halogen) in solution. However, in the crystalline state the complexes with X = Cl and Br (see runs *41* and *42*) have a polymeric structure $\cdots X—X \cdots OC_4H_8O \cdots X—X \cdots OC_4H_8O \cdots$ while in the complex $C_3H_6N_2S \cdots I^1—I^2 \cdots I^3—I^4$ (run *49*) the second iodine molecule, $I^3—I^4$, adds to the 1 : 1 complex through the formation of the $I^2 \cdots I^3$ bond. The length of this bond (3.004 Å) much exceeds the I—I bond length in free iodine molecule (2.67 Å), but is smaller than the sum of the van der Waals radii[122] of two iodine atoms (4.2 Å); this indicates a weak interaction between the $I^3—I^4$ molecule and the $C_3H_6N_2S \cdots I^1—I^2$ complex in the crystal. Ignoring this weak interaction, we included in the data set the enthalpy of formation of the 1 : 1 complex (34 kJ mol^{-1}) determined in solution and the $S \cdots I^1$ bond length in the 1 : 2 complex $C_3H_6N_2S \cdots I^1—I^2 \cdots I^3—I^4$ (2.487 Å). Analogously, we included the enthalpies of formation of the 1 : 1 complexes of 1,4-dioxane with Cl_2 and Br_2 determined in solution (8.8 and 8.4 kJ mol^{-1}, respectively; see Table 1, runs *41* and *42*) and the O···Cl and O···Br bond lengths in the $[1,4\text{-}C_4H_8O_2 \cdot Cl_2]_n$ and $[1,4\text{-}C_4H_8O_2 \cdot Br_2]_n$ complexes (2.67 and 2.71 Å, respectively).

In the rare cases where the enthalpies of complexation were unavailable we used the $-\Delta H$ values of the complexes of related homologs (see runs *8*, *12*, *14*, and *18* in Table 1 and runs *6*, *8*, and *14* in Table 2) assuming that this will not affect the results of our analysis. In addition to the donor-acceptor interaction, other effects, *e.g.*, pπ-conjugation may contribute largely to the enthalpy of formation of certain complexes. These complexes are not included in Tables 1 and 2.

Table 1 lists the gas-phase and crystalline-phase donor-acceptor bond lengths (r_{DA}) determined by microwave spectroscopy (MWS) and X-ray analysis. Analysis of the published data shows that these methods often give similar r_{DA} values provided that the situation in the crystal is not complicated by additional interactions as in, *e.g.*, the dimeric complex $[(CH_3)_3N \cdot AlH_3]_2$ (see Refs 123 and 124) where the Al atoms are linked by two hydrogen bridges. In these cases, no X-ray analysis data were used.

Gas-phase electron diffraction (GED) often overestimates the r_{DA} distances compared to MWS and X-ray

Table 2. Donor-acceptor bond lengths (r_{DA}) obtained by electron diffraction, parameters $\Delta r = r_{DA} - 0.901(r_D + r_A)$,[a] and the enthalpies of formation of molecular complexes ($-\Delta H$)

Run	Complex	r_{DA}	Δr	$-\Delta H$ /kJ mol^{-1} (method)
		Å		
1	$Me_3N \cdot BH_3$	1.656[6]	0.234	132 (CM, gas phase)[7]
2	$Me_3N \cdot BF_3$	1.664[98]	0.242	111 (CM, gas phase)[7]
3	$C_5H_5N \cdot BF_3$	1.669[8]	0.247	104 (CM, benzene)[15]
4	$Me_2O \cdot BF_3$	1.75[99]	0.364	56 (GD)[100]
5	$C_5H_5N \cdot BCl_3$	1.706[8]	0.284	129 (CM, nitrobenzene)[21]
6	$Me_3N \cdot BBr_3$	1.663[101]	0.241	139[b] (CM, benzene)[25]
7	$C_5H_5N \cdot BBr_3$	1.694[8]	0.272	151 (CM, benzene)[25]
8	$Me_3P \cdot BBr_3$	1.946[102]	0.164	168[c] (CM, benzene)[25]
9	$Me_3N \cdot AlMe_3$	2.099[103]	0.335	125 (CM, hexane)[32]
10	$Me_3P \cdot AlMe_3$	2.53[104]	0.406	88 (CM, hexane)[32]
11	$Me_2O \cdot AlMe_3$	2.014[105]	0.286	85 (CM, hexane)[32]
12	$Me_2S \cdot AlMe_3$	2.55[106]	0.480	80 (GD)[107]
13	$H_3N \cdot AlCl_3$	1.996[108]	0.232	133 (GD)[109]
14	$Me_3N \cdot AlCl_3$	1.945[110]	0.181	174[d] (CM, benzene)[111]
15	$H_3N \cdot AlBr_3$	1.997[112]	0.233	140 (GD)[109]
16	$Br_3Sb \cdot AlBr_3$	2.52[113]	0.117	98 (GD)[114]
17	$Me_3N \cdot GaMe_3$	2.09[115]	0.326	88 (GD)[116]
18	$Me_3P \cdot GaMe_3$	2.52[117]	0.396	75 (GD)[118]
19	$Me_2O \cdot GaMe_3$	2.045[119]	0.317	40 (GD)[118]
20	$H_3N \cdot GaCl_3$	2.057[120]	0.293	134 (GD)[121]
21	$H_3N \cdot GaBr_3$	2.081[112]	0.317	137 (GD)[121]

[a] The r_D and r_A values are given in Table 3.
[b] $-\Delta H$ of complex $Et_3N \cdot BBr_3$.
[c] $-\Delta H$ of complex $Bu^n_3P \cdot BBr_3$.
[d] $-\Delta H$ of complex $Et_3N \cdot AlCl_3$.

analysis. For instance, the r_{DA} distances reported for the $Me_3N \cdot BH_3$ complex are 1.609 Å (MWS)[6] and 1.656 Å (GED),[125] whereas the published r_{DA} values in the $C_5H_5N \cdot BF_3$ complex are 1.603 Å (X-ray analysis),[126] 1.610 Å (MWS),[8] and 1.669 Å (GED).[127] The drawbacks of gas-phase electron diffraction can to some extent be reduced by analyzing a combined set of the GED and MWS data (see Ref. 128). The best results were obtained using the SARACEN method (see Refs 128 and 129). Unfortunately, the r_{DA} values determined by this method were not used due to the lack of corresponding thermal effects of complexation reactions. The r_{DA} determined by gas-phase electron diffraction and the thermal effects of corresponding reactions are listed in Table 2.

Undoubtedly, the length of the donor-acceptor bond depends on its strength. However, direct correlations between r_{DA} and the enthalpy of complexation $-\Delta H$ using various functions have failed. This is not surprising because the r_{DA} value is first of all determined by the sizes of the heteroatoms involved in the donor-acceptor bond. The sizes of heteroatoms can differ appreciably. For instance, the covalent radii of the donor heteroatoms (r_D) increase in the order O (0.66 Å) < N (0.7 Å) < S (1.04 Å) < < P (1.1 Å) < Se (1.17 Å) while those of the acceptor heteroatoms (r_A) increase in the order B (0.88 Å) < < Cl (0.99 Å) < Br (1.14 Å) < Al (1.26 Å) = Ga (1.26 Å) < < Ti (1.32 Å) < I (1.33 Å) < Sn (1.38 Å).[122,130]

Clearly, constructing a correct correlation between the donor-acceptor bond lengths and the enthalpies of complexation requires the introduction of corrections for the heteroatom size. To this end, the $r_{DA} - \Sigma r_{cov}$ ($\Sigma r_{cov} = r_D + r_A$ is the sum of the covalent radii of the heteroatoms involved in the donor-acceptor bond) rather than the measured bond lengths (r_{DA}) were used.[4,5] This was done ignoring the polarity of the donor-acceptor bonds (covalent radii are usually calculated using the data for the molecules with homopolar bonds[122,130,131]). But the molecular complexes, in particular, those listed in Tables 1 and 2, are polar compounds. The dipole moments of the donor-acceptor bonds in such complexes often reach 3-4 D (see Ref. 1).

The heteropolar bond is much shorter than the sum of the covalent radii in nonpolar molecules.[130–132] It was proposed[132] to calculate the length of heteropolar bonds by the equation

$$r_{AB} = r_A + r_B - a\Delta X_{AB}, \qquad (4)$$

where r_A and r_B are the covalent radii of the elements A and B, respectively, ΔX_{AB} is the electronegativity difference between these atoms, and $a = 0.09$. In other words, enhancement of bond polarity causes the effective radii of elements to decrease and they become smaller than the covalent radii determined for nonpolar compounds. Clearly, a correction similar to that used in Eq. (4) should also be introduced for the heteroatoms that form the polar donor-acceptor bond. However, the Schomaker—Stevenson[132] equation can hardly be applied to the donor-acceptor bonds; indeed, the electronegativ-

ity of the Al atom in the acceptor $AlCl_3$ should be much higher than the recommended value of 1.5 (see Ref. 122) due to the strong induction effect of three chlorine atoms.[133]

Analysis[131] showed that the measured interatomic distances in the molecules with polar bonds are about 10% shorter than the sum of the covalent radii in the compounds with homopolar covalent bonds. Therefore, we believe that it is more appropriate to use an empirical coefficient at the sum ($r_D + r_A$). In this connection to allow for the size difference between the heteroatoms involved in the polar donor-acceptor bond, we introduced a characteristic parameter Δr calculated as follows

$$\Delta r = r_{DA} - a_1(r_D + r_A), \qquad (5)$$

where a_1 is an empirical coefficient similar to 0.9;[131] r_{DA} is the experimentally determined length of the donor-acceptor bond, and r_D and r_A are respectively the donor and acceptor covalent atomic radii according to L. Pauling;[130] for the covalent radii of octahedral complexes of tin, titanium, and antimony not available from L. Pauling we used the values recommended by S. Batsanov.[122] The Δr value thus obtained was then used for constructing a correlation with $-\Delta H$. Physically, the product $a_1(r_D + r_A)$ is the sum of the covalent radii for the heteropolar bonds. Table 3 presents the numerical values of the homopolar covalent radii used in our calculations and the geometry of the environment of the acceptor atom involved in the donor-acceptor bond, which was used for choosing the corresponding r_A values.

Table 1 presents the enthalpies of formation ($-\Delta H$) of almost sixty molecular complexes and the corresponding r_{DA} values determined by MWS and X-ray analysis. Regression analysis of these data (calculated using the STATGRAPHICS 5.1 program) revealed that the correlation between the enthalpies $-\Delta H$ and the experimental

Table 3. Covalent radii of heteroatoms donors (r_D) and heteroatoms acceptors (r_A) that form the donor-acceptor bonds in the complexes listed in Tables 1 and 2

Donor	r_D/Å[130]	Acceptors	Complex composition (geometry)	r_A/Å
>N:	0.7	BX_3,[a] BH_3, BR_3	1 : 1 (tetrahedron)	0.88[130]
>N:				
—C≡N:	0.53	AlX_3, AlR_3, GaX_3, GaR_3	1 : 1 (tetrahedron)	1.26[130]
>P:	1.1	TiX_4	2 : 1 (octahedron)	1.32[122]
>O:	0.66	NbX_5	1 : 1 (octahedron)	1.40[122]
>S:	1.04	SnX_4, R_2SnX_2, R_3SnX	2 : 1 (octahedron)	
			1 : 1 (trigonal bipyramid)[b]	1.38[122]
>Se:	1.17	SbX_3	2 : 1 (square pyramid)[c]	1.36[130]
>Sb:	1.41	SbX_5	1 : 1 (octahedron)	1.43[122]
>P=O:	0.55	SO_2	1 : 1[d]	1.04[130]
>S=O:				
>Se=O:				
>P=S:	0.94	Cl_2	1 : 1 (linear)	0.99[130]
>C=S:				
>P=Se:	1.07	Br_2	1 : 1 (linear)	1.14[130]
		I_2, ICl, IBr	1 : 1 (linear)	1.33[130]

[a] X is halogen.
[b] No data for this geometry are available; the r_A value for octahedral complexes of tin was accepted.
[c] No data for this geometry are available, the r_A value for tetrahedral complexes of antimony was accepted.
[d] The geometry of the complex can be found in Ref. 66.

values of the donor-acceptor bond length r_{DA} and the covalent radii of heteroatoms (r_D and r_A, see Table 3) has the form

$$-\Delta H = a_2/[r_{DA} - a_1(r_D + r_A)], \quad (6)$$

where $a_1 = 0.901 \pm 0.007$, $a_2 = 21.6 \pm 1.6$ kJ Å mol^{-1} (hereafter the confidence interval is given at a probability level of 0.95), the correlation coefficient is 0.97, and the mean average relative error of approximation for $-\Delta H$ is 15%.

The numerical value of the coefficient a_1 is in excellent agreement with the predicted[131] magnitude (10%) of the decrease in the sum of the covalent radii on going from homopolar to heteropolar bonds. This indicates the correctness of our approach that makes it possible to determine the lengths of the donor-acceptor bonds formed by different sets of heteroatoms having strongly different covalent radii using the parameter Δr calculated from Eq. (5). The theoretical Δr values for $a_1 = 0.901$ are given in Tables 1 and 2. It follows that $-\Delta H$ and Δr are related by a hyperbolic function

$$-\Delta H = a_2/\Delta r, \quad (7)$$

where $a_2 = 21.6$ kJ Å mol^{-1}.

Figure 1, *a* presents a graphical illustration of the quality of our description; here filled triangles denote the experimental data and the solid line represents the results of calculations using Eq. (7). The experimental points corresponding to the nv- and nσ-type complexes differing in composition, coordination number, and the nature of electron donors (amines, ethers, sulfides, oxo compounds, *etc.*) and electron acceptors (compounds of boron, aluminum, tin, titanium, iodine, *etc.*) fall on the curve with a reasonable accuracy. Thus, the correlation obtained (see Eq. (7)) has a general character and is independent of the nature of the constituents of the molecular complex.

Figure 1, *b* presents the theoretical curve plotted using the MWS and X-ray analysis data and the points corresponding to the Δr values calculated with the r_{DA} distances determined by gas-phase electron diffraction (see Table 2). The GED data show a much larger scatter compared with the MWS and X-ray analysis data (see Fig. 1, *a*) and in most cases lie on the right of the theoretical curve. We believe this is due to the fact that gas-phase electron diffraction gives somewhat overestimated r_{DA} values compared to MWS and X-ray analysis. At the same time combined regression analysis of the data listed in Tables 1 and 2 using Eqn. (7) gives $a_2 = 23.2 \pm 1.4$ kJ Å mol^{-1}, for which the confidence interval overlaps with that of a_2 determined by processing only the MWS and X-ray analysis data ($a_2 = 21.6 \pm 1.6$ kJ Å mol^{-1}). But in this case the correlation coefficient decreases from 0.97 to 0.85, *i.e.*, there is no correlation according to known classification.[133] Seemingly, gas-phase electron diffraction (drawbacks of the technique were considered in Refs 128 and 129) is inappropriate for constructing correlations with the enthalpies of complexation in the fashion we have proposed.

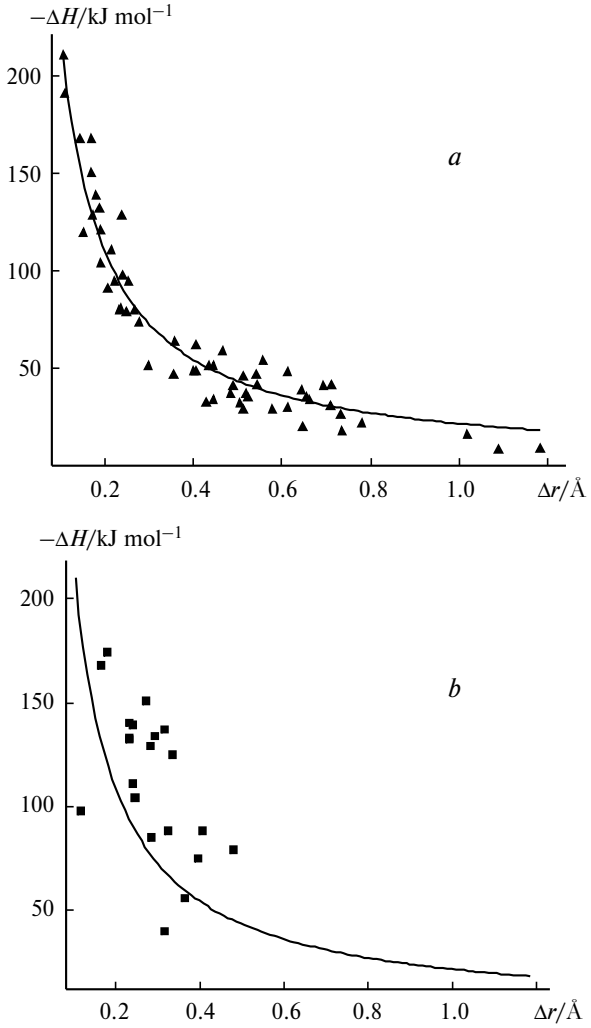

Fig. 1. Enthalpies of formation of molecular complexes ($-\Delta H$) plotted *vs.* characteristic parametet Δr. Points denote experimental data; the Δr values were calculated using the r_{DA} determined by X-ray analysis and microwave spectroscopy (*a*; see Table 1) and by gas-phase electron diffraction (*b*; see Table 2); the solid curve was calculated using Eq. (7).

Mention should be made of yet another source of possible errors in the correlation between $-\Delta H$ and Δr. The energy of the donor-acceptor bond equals the enthalpy of complexation only if the energies of structural rearrangements in the donor and acceptor constituents of the complex are low. Otherwise, the enthalpy of complexation is lower than the energy of the donor-acceptor bond. Examples are provided by the complexes whose formation requires energy expenditure for violation of pπ-conjugation. The pπ-conjugation energy depends on the character of the heteroatom, the number of phenyl

rings, steric effects and can be rather high, for instance, 61 kJ mol^{-1} for *N*-methyldiphenylamine, 29 kJ mol^{-1} for triphenylphosphine, 26 kJ mol^{-1} for anisole, and 23 kJ mol^{-1} for diphenyl sulfide.[134] Therefore, the point corresponding to complexes of such electron donors will fall below the curve shown in Fig. 1,*a*. At the same time the point corresponding to, *e.g.*, the $HC(O)NMe_2 \cdot SbCl_5$ complex should lie above this curve, because the formation of this complex is accompanied by additional energy gain due to the strengthening of the resonance interaction between the lone electron pair of the nitrogen atom and the π-system of the C=O bond (see Ref. 135).

The plot in Fig. 1, *a* shows that as the binding energies of the complexes increase the length of the donor-acceptor bond tends to the sum of the heteropolar covalent radii of the atoms involved in this bond (Δr tends to zero). Contrary to this, at $\Delta r \gg 1$ the bond weakens and the $-\Delta H$ values tend to zero. The situation (see Fig. 1, *a*) has a clear physical meaning, namely, it is determined by the ratio of the contributions of the charge-transfer forces and the classical intermolecular forces (Coulomb, dipole-dipole, dipole-induced dipole interactions, *etc*.) to the complexation energy. At small Δr, the charge-transfer forces dominate; however, an increase in the distance between the donor and acceptor molecules causes this contribution to decrease and weak van der Waals forces now play an increasingly important role. Nevertheless, charge transfer still contributes largely even to the weakest complexes studied, that is, the complexes of halogens with dioxane (Δr = 1—1.2 Å, $-\Delta H$ = 8—16 kJ mol^{-1}). The necessary condition for the formation of this bond is the orbital overlap between the donor and acceptor heteroatoms.[1,2,136] Therefore, the length of a donor-acceptor bond should be smaller than the sum of the van der Waals radii (Σr_{VWR}) of the heteroatoms involved in this bond. Indeed, the O—X bond lengths in the X_2 (X = Cl, Br, I) complexes with 1,4-dioxane are respectively 2.67, 2.71, and 2.81 Å, which is smaller than the corresponding Σr_{VWR} values for the oxygen and chlorine, bromine, and iodine atoms equal to 3.3, 3.4 and 3.6 Å, respectively (see Ref. 122). At the same time the dipole moments of halogen molecules are equal to zero, while the repeatedly measured dipole moment of 1,4-dioxane varies from 0 to 0.4 D depending on the temperature and solvent. Nevertheless, almost non-dipole halogen and 1,4-dioxane molecules form complexes having dipole moments μ of the order of 1.3 D;[1,137] this is due to charge transfer from the donor to acceptor.

References

1. E. N. Guryanova, I. P. Goldstein, and I. P. Romm, *Donor-Acceptor Bond,* Wiley, New York, 1975, 366 pp.
2. R. S. Mulliken and W. B. Person, *Molecular Complexes*, Wiley, New York, 1969, 498 pp.
3. R. G. Pews, Y. Tsuno, and R. W. Taft, *J. Am. Chem. Soc.*, 1967, **89**, 2391.
4. E. N. Guryanova, *Zh. Strukt. Khim.*, 1975, **16**, 143 [*J. Struct. Chem. (USSR)*, 1975, **16** (Engl. Transl.)].
5. E. N. Guryanova and I. P. Romm, *Khim. Fiz.*, 1992, **11**, 795 [*Chem. Phys.*, 1992, **11** (Engl. Transl.)].
6. J. R. Durig, Y. S. Li, and J. D. Odom, *J. Mol. Struct.*, 1973, **16**, 443.
7. A. Shepp and S. H. Bauer, *J. Am. Chem. Soc.*, 1954, **76**, 265.
8. W. Caminati and D. Damiani, *J. Mol. Struct.*, 1986, **147**, 389.
9. H. C. Brown and L. Domash, *J. Am. Chem. Soc.*, 1956, **78**, 5384.
10. P. M. Kuznesof and R. L. Kuczkowski, *Inorg. Chem.*, 1978, **17**, 2308.
11. H. C. Brown, H. Bartholomay, and M. D. Taylor, *J. Am. Chem. Soc.*, 1944, **66**, 435.
12. K. Ouzounis, H. Riffel, and H. Hess, *J. Organomet. Chem.*, 1987, **332**, 253.
13. D. C. Bradley, M. B. Hursthouse, M. Motevalli, and Dao-Hong Zheng, *J. Chem. Soc., Chem. Commun.*, 1991, 7.
14. P. Cassoux, R. L. Kuczkowski, and A. Serafini, *Inorg. Chem.*, 1977, **16**, 3005.
15. I. P. Romm, T. G. Sevastyanova, E. N. Guryanova, I. D. Kolli, and R. A. Rodionov, *Zh. Obshch. Khim.*, 1968, **38**, 1938 [*J. Gen. Chem. USSR*, 1968, **38** (Engl. Transl.)].
16. U. Monkowius, S. Nogai, and H. Schmidbauer, *J. Chem. Soc., Dalton Trans.*, 2003, 987.
17. H. C. Brown, *J. Chem. Soc.*, 1956, 1248.
18. I. Lindqvist, *Inorganic Adduct Molecules of Oxo-Compounds*, Springer-Verlag, Berlin, 1963, 129 pp.
19. P. C. Maria and J. F. Gal, *J. Phys. Chem.*, 1985, **89**, 1296.
20. K. Topel, K. Hensen, and M. Tromel, *Acta Crystallogr., Sect. B*, 1981, **B37**, 969.
21. H. C. Brown and R. R. Holmes, *J. Am. Chem. Soc.*, 1956, **78**, 2173.
22. O. Conrad, C. Jansen, and B. Krebs, *Angew. Chem., Int. Ed. Engl.*, 1998, **37**, 3209.
23. H. L. Morris, N. Kulevsky, M. Tamres, and S. Searles, *Inorg. Chem.*, 1966. **5**, 124.
24. P. H. Clippard, J. C. Hanson, and R. C. Taylor, *J. Cryst. Mol. Struct.*, 1971, **1**, 363.
25. I. P. Romm, Zh. S. Galuashvili, and E. N. Guryanova, *Zh. Obshch. Khim.*, 1976, **46**, 2445 [*J. Gen. Chem. USSR*, 1976, **46** (Engl. Transl.)].
26. K. Iijima, J. Oonishi, and S. Shibata, *Chem. Lett.*, 1983, 251.
27. D. L. Black and R. C. Taylor, *Acta Crystallogr., Sect. B*, 1975, **B31**, 1116.
28. C. Aubauer, K. Davidge, T. M. Klapotke, P. Mayer, H. Piotrowski, and A. Schulz, *Z. Anorg. Allg. Chem.*, 2000, **626**, 2373.
29. I. P. Goldshtein, A. N. Fedotov, I. A. Misurkin, and E. N. Guryanova, *Zh. Obshch. Khim.*, 1986, **56**, 40 [*J. Gen. Chem. USSR*, 1986, **56** (Engl. Transl.)].
30. I. P. Goldshtein, E. N. Guryanova, L. V. Kucheruk, and E. D. Kremer, *Zh. Obshch. Khim.*, 1978, **48**, 2568 [*J. Gen. Chem. USSR*, 1978, **48** (Engl. Transl.)].
31. D. C. Bradley, G. Coumbarides, J. S. Harding, G. E. Hawkes, J. A. Maia, and M. Motevalli, *J. Chem. Soc., Dalton Trans.*, 1999, 3553.
32. C. H. Henrickson, D. Duffy, and D. P. Eyman, *Inorg. Chem.*, 1968, **7**, 1047.

33. N. Burford, B. W. Royan, R. Spence, T. S. Cameron, A. Linden, and R. D. Rogers, *J. Chem. Soc., Dalton Trans.*, 1990, 1521.
34. I. P. Romm, E. N. Guryanova, V. M. Ryaboi, and E. P. Buchikhin, *Zh. Obshch. Khim.*, 1979, **49**, 2098 [*J. Gen. Chem. USSR*, 1979, **49** (Engl. Transl.)].
35. N. Burford, A. D. Phillips, R. W. Schurko, R. E. Wasylschen, and J. F. Richardson, *J. Chem. Soc., Chem. Commun.*, 1997, 2363.
36. A. V. Suvorov and V. L. Shubaev, *Zh. Neorg. Khim.*, 1971, **16**, 318 [*J. Inorg. Chem. USSR*, 1971, **16** (Engl. Transl.)].
37. M. Webster and H. E. Blayden, *J. Chem. Soc. A.*, 1969, 2443.
38. Y. Farhangi and D. P. Graddon, *Inorg. Chim. Acta*, 1987, **133**, 239.
39. A. V. Yatsenko, L. A. Aslanov, M. Yu. Burtsev, and E. A. Kravchenko, *Zh. Neorg. Khim.*, 1991, **36**, 2031 [*J. Inorg. Chem. USSR*, 1991, **36** (Engl. Transl.)].
40. N. A. Morozova, Yu. V. Kondrat´ev, A. V. Suvorov, and V. N. Osokin, *Vestn. LGU* [*Leningrad State Univ. Bull.*], 1983, Iss. 4, 108 (in Russian).
41. L. A. Aslanov, V. M. Attiya, V. M. Ionov, A. B. Permin, and V. S. Petrosyan, *Zh. Strukt. Khim.*, 1977, **18**, 1113 [*J. Struct. Chem. (USSR)*, 1977, **18** (Engl. Transl.)].
42. T. F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, 1966, **88**, 3921.
43. S. W. Ng and V. G. Kumar Das, *Acta Crystallogr., Sect. C*, 1992, **C48,** 1839.
44. J. N. Spencer, R. B. Belser, and S. R. Moyer, *Organometallics*, 1986, **5**, 118.
45. L. A. Aslanov, V. M. Ionov, V. M. Attiya, A. B. Permin, and V. S. Petrosyan, *Zh. Strukt. Khim.*, 1978, **19**, 185 [*J. Struct. Chem. (USSR)*, 1978, **19** (Engl. Transl.)].
46. Y. Farhangi and D. P. Graddon, *J. Organomet. Chem.*, 1975, **87**, 67.
47. E. A. Blom, B. R. Penfold, and W. T. Robinson, *J. Chem. Soc. A*, 1969, 913.
48. D. P. Graddon and B. A. Rana, *J. Organomet. Chem.*, 1977, **136**, 19.
49. L. A. Aslanov, V. M. Ionov, W. M. Attia, A. B. Permin, and V. S. Petrosyan, *J. Organomet. Chem.*, 1978, **144**, 39.
50. H. Fujiwara, F. Sakai, Y. Mikawa, and Y. Sasaki, *Bull. Chem. Soc. Jpn*, 1985, **58**, 1741.
51. P. G. Harrison, T. J. King, and J. A. Richards, *J. Chem. Soc., Dalton Trans.*, 1974, 1723.
52. D. Canningham, E. M. Landers, P. McArdle, and N. N. Chonchubhair, *J. Organomet. Chem.*, 2000, **612**, 53.
53. J. N. Spencer, T. F. Gannis, A. I. Zafar, C. M. Salata, S. Gupta, S. Puppalatu, H. J. Eppley, J. L. Ealy, and C. H. Yoder, *J. Phys. Chem.*, 1991, **95**, 4910.
54. K. A. Paseshnichenko, L. A. Aslanov, A. V. Yatsenko, and S. V. Medvedev, *Koord. Khim.*, 1984, **10**, 1279 [*Sov. J. Coord. Chem.*, 1984, **10** (Engl. Transl.)].
55. Y. Farhangi and D. P. Graddon, *J. Organomet. Chem.*, 1986, **317**, 153.
56. S. I. Troyanov, G. N. Mazo, V. B. Rybakov, and K. V. Budkina, *Koord. Khim.*, 1990, **16**, 466 [*Sov. J. Coord. Chem.*, 1990, **16** (Engl. Transl.)].
57. T. N. Sevastyanova and A. V. Suvorov, *Koord. Khim.*, 1997, **23**, 812 [*Russ. J. Coord. Chem.*, 1997, **23** (Engl. Transl.)].
58. C. I. Branden and I. Lindqvist, *Acta Chem. Scand.*, 1963, **17**, 353.
59. A. V. Suvorov, A. M. German, and N. P. Bondareva, *Zh. Neorg. Khim.,* 1971, **16**, 2413 [*J. Inorg. Chem. USSR*, 1971, **16** (Engl. Transl.)].
60. A. Lipka and H. Wunderlich, *Z. Naturforsch.*, *Teil B*, 1980, **35b**, 1548.
61. M. J. Gallagher, D. P. Graddon, and A. R. Sheikh, *Thermochim. Acta.*, 1978, **27**, 269.
62. L. Golic and S. Milicev, *Acta Crystallogr., Sect. B.*, 1978, **B34**, 3379.
63. H. Binas, *Z. Anorg. Allg. Chem.*, 1967, **352**, 271.
64. V. Gutmann, A. Steininger, and E. Wychera, *Monatsh. Chem.*, 1966, **97**, 460.
65. Y. Hermodsson, *Acta Chem. Scand.*, 1967, **21**, 1313.
66. J. J. Oh, M. S. LaBarge, J. Matos, J. W. Kampf, K. W. Hillig, and R. L. Kuczkowski, *J. Am. Chem. Soc.*, 1991, **113**, 4732.
67. J. Grundnes and S. D. Christian, *J. Am. Chem. Soc.*, 1968, **90**, 2239.
68. O. Hassel and K. O. Stromme, *Acta Chem. Scand.*, 1959, **13**, 1775.
69. Yu. A. Serguchev and G. A. Stetsyuk, *Ukr. Khim. Zh.* [*Ukr. Chem. J.*], 1973, **39**, 96 (in Russian).
70. O. Hassel and J. Hvoslef, *Acta Chem. Scand.*, 1954, **8**, 873.
71. Yu. A. Serguchev and E. A. Shilov, *Teor. Eksp. Khim.*, 1970, **6**, 680 [*Theor. Exp. Chem.*, 1970, **6** (Engl. Transl.)].
72. O. Hassel, *Mol. Phys.*, 1958, **1**, 241.
73. H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Jpn*, 1960, **33**, 1660.
74. O. Hassel, C. Romming, and T. Tufte, *Acta Chem. Scand.*, 1961, **15**, 967.
75. V. C. Krishna and B. B. Bhowmik, *J. Am. Chem. Soc.*, 1968, **90**, 1700.
76. O. Hassel, *Acta Chem. Scand.*, 1965, **19**, 2259.
77. A. F. Garito and B. B. Wayland, *J. Phys. Chem.*, 1967, **71**, 4062.
78. O. Hassel, *Proc. Chem. Soc.*, *London*, 1957, 250.
79. I. G. Arzamanova, E. N. Guryanova, and I. P. Goldshtein, *Dokl. Akad. Nauk SSSR*, 1964, **155**, 1391 [*Dokl. Chem.*, 1964 (Engl. Transl.)].
80. G. Y. Chao and J. D. McCullough, *Acta Crystallogr.*, 1960, **13**, 727.
81. J. D. McCullough and I. C. Zimmermann, *J. Phys. Chem.*, 1961, **65**, 888.
82. F. Bigoli, P. Deplako, A. Ienco, C. Mealli, M. L. Mercuri, M. A. Pellinghelli, G. Pintus, G. Saba, and E. F. Trogu, *Inorg. Chem.*, 1999, **38**, 4626.
83. F. H. Herbstein and W. Schwotzer, *J. Am. Chem. Soc.*, 1984, **106**, 2367.
84. R. Abu-Eittah and A. El-Kourashy, *J. Phys. Chem.*, 1972, **76**, 2405.
85. D. C. Apperley, N. Bricklebank, S. L. Burns, D. E. Hibbs, M. B. Hursthouse, and K. M. A. Malik, *J. Chem. Soc., Dalton Trans.*, 1998, 1289.
86. F. Lux, R. Paetzold, J. Danel, and L. Sobczyk, *J. Chem. Soc., Faraday Trans. 2*, 1975, **71**, 1610.
87. W. I. Cross, S. Godfrey, S. L. Jackson, C. A. McAuliffe, and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1999, 2225.
88. P. Bruno, M. Caselli, C. Fragale, and S. Magrino, *J. Inorg. Nucl. Chem.*, 1977, **39**, 1757.
89. H. Hope and J. D. McCullough, *Acta Crystallogr.*, 1964, **17**, 712.

90. J. D. McCullough and A. Brunner, *Inorg. Chem.*, 1967, **6**, 1251.
91. Y. G. Chao and J. D. McCullough, *Acta Crystallogr.*, 1961, **14**, 940.
92. C. Knobler and J. D. McCullough, *Inorg. Chem.*, 1968, **7**, 365.
93. S. M. Godfrey, S. L. Jackson, C. A. McAuliffe, and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1997, 4499.
94. D. V. Muravlyanskii, E. N. Guryanova, I. P. Romm, B. D. Sviridov, and E. S. Shcherbakova, *Zh. Obshch. Khim.*, 1986, **56**, 1299 [*J. Gen. Chem. USSR*, 1986, **56** (Engl. Transl.)].
95. T. Dahl, O. Hassel, and K. Sky, *Acta Chem. Scand.*, 1967, **21**, 592.
96. J. R. Masaguer, A. Sousa-Alonso, J. A. Garcia-Vazquez, and A. Blanco, *Rev. Roum. Chim.*, 1978, **23**, 1409.
97. H. P. Sieper and R. Paetzold, *Z. Phys. Chem.* (*Leipzig*), 1974, **225**, 1125.
98. M. Hargittai and I. Hargittai, *J. Mol. Struct.*, 1977, **39**, 79.
99. K. Iijima, T. Yamada, and S. Shibata, *J. Mol. Struct.*, 1981, **77**, 271.
100. H. C. Brown and R. M. Adams, *J. Am. Chem. Soc.*, 1942, **64**, 2557.
101. K. Iijima and S. Shibata, *Bull. Chem. Soc Jpn.*, 1980, **53**, 1908.
102. K. Iijima, E. Koshimizu, and S. Shibata, *Bull. Chem. Soc. Jpn*, 1981, **54**, 2255.
103. G. A. Anderson, F. R. Forgaard, and A. Haaland, *Acta Chem. Scand.*, 1972, **26**, 1947.
104. A. Almenningen, L. Fernholt, and A. Haaland, *J. Organomet. Chem.*, 1978, **145**, 109.
105. A. Haaland, S. Samdal, O. Stokkeland, and J. Weidlein, *J. Organomet. Chem.*, 1977, **134**, 165.
106. L. Fernholt, A. Haaland, M. Hargittai, R. Seip, and J. Weidlein, *Acta Chem. Scand. Ser. A*, 1981, **A35**, 529.
107. N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, 1942, **64**, 316.
108. M. Hargittai, I. Hargittai, V. P. Spiridonov, M. Pelissier, and J. F. Labarre, *J. Mol. Struct.*, 1975, **24**, 27.
109. V. I. Trusov and A. V. Suvorov, *Zh. Neorg. Khim.*, 1974, **19**, 3253 [*J. Inorg. Chem. USSR*, 1974, **19** (Engl. Transl.)].
110. A. Almenningen, A. Haaland, T. Haugen, and D. P. Novak, *Acta Chem. Scand.*, 1973, **27**, 1821.
111. I. P. Romm, S. V. Moshchenok, L. P. Ivanov, E. N. Guryanova, and A. I. Gorbunov, *Zh. Obshch. Khim.*, 1986, **56**, 27 [*J. Gen. Chem. USSR*, 1986, **56** (Engl. Transl.)].
112. M. Hargittai, I. Hargittai, V. P. Spiridonov, and A. A. Ivanov, *J. Mol. Struct.*, 1977, **39**, 225.
113. V. P. Spiridonov and A. S. Malkova, *Zh. Strukt. Khim.*, 1969, **10**, 332 [*J. Struct. Chem. (USSR)*, 1969, **10** (Engl. Transl.)].
114. A. V. Suvorov, A. S. Malkova, and V. I. Avronina, *Zh. Neorg. Khim.*, 1969, **14**, 1374 [*J. Inorg. Chem. USSR*, 1969, **14** (Engl. Transl.)].
115. V. S. Mastryukov, V. P. Novikov, L. V. Vilkov, A. V. Golubinskii, L. M. Golubinskaya, and V. I. Bregadze, *Zh. Strukt. Khim.*, 1987, **28**, 143 [*J. Struct. Chem. (USSR)*, 1987, **28** (Engl. Transl.)].
116. G. E. Coates, *Organometallic Compounds*, Wiley, New York, 1960. 366 p.
117. L. M. Golubinskaya, A. V. Golubinskii, V. S. Mastryukov, L. V. Vilkov, and V. I. Bregadze, *J. Organomet. Chem.*, 1976, **117**, C4.
118. G. E. Coates, *J. Chem. Soc.*, 1951, 2003.
119. V. P. Novikov, A. V. Golubinskii, V. S. Mastryukov, L. V. Vilkov, L. M. Golubinskaya, and V. I. Bregadze, *Zh. Strukt. Khim.*, 1985, **26**, 34 [*J. Struct. Chem. (USSR)*, 1985, **26** (Engl. Transl.)].
120. M. Hargittai, I. Hargittai, and V. P. Spiridonov, *J. Mol. Struct.*, 1976, **30**, 31.
121. A. Yu. Timoshkin, A. V. Suvorov, and G. F. Shefer, *Zh. Obshch. Khim.*, 1999, **69**, 1250 [*Russ. J. Gen. Chem.*, 1999, **69** (Engl. Transl.)].
122. S. S. Batsanov, *Zh. Neorg. Khim.*, 1991, **36**, 3015 [*J. Inorg. Chem. USSR*, 1991, **36** (Engl. Transl.)].
123. J. L. Atwood, F. R. Bennett, C. L. Elms, C. Jones, C. L. Raston, and K. D. Robinson, *J. Am. Chem. Soc.*, 1991, **113**, 8183.
124. C. Y. Tang, R. A. Coxall, A. J. Downs, T. M. Green, and S. Parsons, *J. Chem. Soc., Dalton Trans.*, 2001, 2141.
125. K. Iijima, N. Adachi, and S. Shibata, *Bull. Chem. Soc. Jpn*, 1984, 3269.
126. K. Topel, K. Hensen, and J. W. Bats, *Acta Crystallogr. Sect. C.*, 1984, **C40**, 828.
127. K. Iijima, T. Noda, M. Maki, T. Sasase, and S. Shibata, *J.Mol. Struct.*, 1986, **144**, 169.
128. P. T. Brain, H. E. Brown, A. J. Downs, T. M. Green, E. Johnsen, S. Parsons, D. W. H. Renkin, B. A. Smart, and C. Y. Tang, *J. Chem. Soc., Dalton Trans.*, 1998, 3685.
129. C. Y. Tang, R. A. Coxall, A. J. Downs, T. M. Green, L. Kettle, S. Parsons, D. W. H. Rankin, H. F. Robertson, and A. R. Turner, *J. Chem. Soc., Dalton Trans.,* 2003, 3526.
130. L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, 1960, 680 pp.
131. J. A. Campbell, *Chemical Systems, V. 1*, W. H. Freeman and Company, San Francisco, 1970.
132. V. Schomaker and D. Stevenson, *J. Am. Chem. Soc.*, 1941, **63**, 37.
133. Yu. A. Zhdanov and V. I. Minkin, *Korrelyatsionnyi analiz v organicheskoi khimii* [*Correlation Analysis in Organic Chemistry*], Izd. Rostov-on-Don Univ., Rostov-on-Don, 1966, 470 pp. (in Russian).
134. I. P. Romm and E. N. Guryanova, *Usp. Khim.*, 1986, **55**, 225 [*Russ. Chem. Rev.*, 1986, **55** (Engl. Transl.)].
135. L. A. Ganyushin, I. P. Romm, E. N. Guryanova, E. S. Isaeva, V. M. Ryaboi, and E. S. Shcherbakova, *Zh. Obshch. Khim.*, 1980, **50**, 2159 [*J. Gen. Chem. USSR*, 1980, **50** (Engl. Transl.)].
136. S. F. Mason, *Quart. Rev.*, 1961, **15**, 287.
137. Ya. K. Syrkin and K. M. Anisimova, *Dokl. Akad. Nauk SSSR,* 1948, **59**, 1457 [*Dokl. Chem.*, 1948 (Engl. Transl.)].

Received June 15, 2007;
in revised form July 22, 2007