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THE STUDY OF CHARGE-TRANSFER COMPLEXES OF ARENETRICARBONYL-CHROMIUM, -MOLYBDENUM AND -TUNGSTEN DERIVATIVES WITH VARIOUS π-ACCEPTORS BY ELECTRONIC ABSORPTION SPECTROSCOPY

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Summary

The charge-transfer complexes of arenetricarbonyl-chromium, -molybdenum and -tungsten with various π-acceptors (tetracyanoethylene, trinitrobenzene, chloranil, bromanil, trinitrophenol) were investigated by electronic absorption spectroscopy. It was shown that (a) molecular arenetricarbonylchromium complexes with tetracyanoethylene are of π, π-type; (b) the character of the donor—acceptor interaction of the tricarbonylchromium group with arene depends on the positive charge value on the ring, identifiable by the electron affinity of the acceptor. In particular, for the relatively strong π-acceptor tetracyanoethylene the group $Cr(CO)_3$ is an electron-donor with respect to the benzene ring and is an electron-acceptor for trinitrobenzene.

Introduction

Electronic absorption spectroscopy of charge-transfer (CT) complexes of the π, π-type is the most valuable method for the investigation of the interaction between substituents and an aromatic ring with a significant positive charge in the charge-transfer state. This method has been used earlier for the investigation of charge-transfer complexes of organic and organometallic benzene [1], naphthalene [2], thiophene [3] and furan [4] derivatives.

In a number of works [5—8] charge-transfer complexes of arenetricarbonyl-chromium, -molybdenum and -tungsten derivatives with 1,3,5-trinitrobenzene (TNB) and tetracyanoethylene (TCNE) as π-acceptors were investigated by electronic absorption spectroscopy. In combination with other methods, valuable information was obtained on the electronic structure of these transition metal π-complexes and it was shown that the electronic structure of the aromatic compound being incorporated as a ligand into the arenetricarbonylmetal molecule undergoes substantial changes [9]. The transition from arene to arenetricarbonylmetal may be considered as an introduction of a not normally organometallic π-bonded $Cr(CO)_3$ substituent into the arene. It is of interest to further investigate the arene electron-donor property changes following the introduction of this substituent. Also the structure of CT arenetricarbonyl complexes with such a characteristic π-acceptor as tetracyanoethylene remains to be investigated [6,8]. From our point of view the additional information on electronic effects in arenetricarbonylmetals may be obtained by means of investigation of their CT complexes with various π-acceptors which differing substantially in electron affinity, but possessing similar molecular structure. We chose tetracyanoethylene(TCNE)(1.8), bromanil(BA)(1.6), chloranil(CA)(1.5), trinitrophenol(TNP)(~1) and trinitrobenzene(TNB)(0.7) as such acceptors. The electron affinity values E_A reported in ref. 10 are given in parentheses. For the TNP molecule an estimated value is given. The results of the electron absorption study of CT arenetricarbonylmetal complexes are summarized in Tables 1 and 2.

Results and discussion

First of all let us consider the charge-transfer frequency values in the electronic absorption spectra of CT complexes of arenes with TCNE and the corresponding arenetricarbonylchromium with TNB and TCNE. The data from Table 1 indicate that the charge-transfer frequency values ν(CT) in arenes change symbatically with the σ_p^+-constant values of substituents on the ring (in the case of multiple substitution the sum of σ_p^+-constants is taken). The lower values of σ_p^+ (pronounced electron-donor properties of substituents in the charge-transfer state) correspond to lower ν(CT) values. According to Mulliken's theory of electron-donor-acceptor complexes [11], the introduction of the electron-donor substituent into the benzene ring leads to stabilization of both ground and excited states of the complex, with the latter stabilizing to a greater degree. This results in a decrease of the charge-transfer energy (ν(CT) frequencies) and the shift of the CT band towards the longer wavelength region.

A similar situation is observed for arenetricarbonylchromium molecular complexes (MC) with TNB (the penultimate column in Table 1, where both our and literature data are presented). Indeed, coordination with the $Cr(CO)_3$ group has little influence on the conjugation of the phenyl ring with substituents, but the inductive component of the $(CO)_3CrC_6H_5$ fragment polar influence greatly increases [12]. Thus the introduction of the $Cr(CO)_3$ group is equivalent to the introduction of a strong electron-acceptor on the ring and this is supported by the literature data. It is known, for instance, that the pK_a of phenylacetic acid coordinated to tricarbonylchromium is as high as that of *p*-nitrophenylacetic acid; at the same time benzoic acid containing an $Cr(CO)_3$ group is a stronger acid than unsubstituted benzoic acid and anilinetricarbonylchromium is a weaker base than aniline. According to X-ray data for the anizoltricarbonylchromium-TNB complex [15,16] the ring plane of the aromatic molecule which is a part of MC and the plane formed by oxygen atoms

TABLE 1

CHARGE TRANSFER FREQUENCIES (ν(CT)) IN CT ARENETRICARBONYLCHROMIUM COMPLEXES SPECTRA WITH VARIOUS ACCEPTORS

Number	arene	ν(CT TCNE) [a] $\times 10^{-2}$ (cm^{-1})	π-arene Cr(CO)$_3$					$\Sigma\sigma_p^+$
			charge transfer frequency ν(CT) $\times 10^{-2}$ (cm^{-1})					
			TCNE	BA	CA	TNP	TNB	
1	$C_6H_5NH_2$	164	167					−2.8
2	$C_6(CH_3)_6$	185	157					−1.9
3	$C_6H_5N(CH_3)_2$	159	167	225	228	224	189 [b]	−1.7
4	$C_6H_2(CH_3)_4$-I,2,4,5	208	150					−1.2
5	$C_6H_3(CH_3)_3$-I,3,5	217	143				198 [b]	−0.9
6	$C_6H_5OCH_3$	232.5	143	217	216	217	201 [b]	−0.8
7	o-$C_6H_4(CH_3)_2$	196	139				200 [b]	−0.6
8	m-$C_6H_4(CH_3)_2$	227.5	140					−0.6
9	p-$C_6H_4(CH_3)_2$	241	143	222	224	221		−0.6
10	$C_6H_5C_2H_5$	242.5	144	222	221	225	200	−0.31
11	$C_6H_5CH_3$	246	141		220	220	202 [b]	−0.3
12	$(C_6H_5)_4Ge$	240	138					−0.15
13	$C_6H_5Ge(C_2H_5)_3$		139					
14	C_6H_5F	278	127	215		218		−0.1
15	$C_6H_5Si(C_2H_5)_3$	250	137					0.0
16	C_6H_6	260	136	215	220	211	205 [b]	0.0
17	C_6H_5Cl	264	128	220	220		213	+0.1
18	C_6H_5J	223	138					+0.13
19	C_6H_5COOH	270	123 [b]					+0.4
20	$C_6H_5COOCH_3$	270	121 [b]					+0.45
21	$C_6H_5COOC_2H_5$	272 [a]	125					+0.5

[a] Ref. 8 data. [b] Ref. 6 data.

of the CO groups are approximately parallel to the plane of the aromatic acceptor molecule. Because of the small value of the overlap integral, the probability of coordination of the TNB molecule with the central metal atom and CO groups is negligible. Nonetheless Fischer et al. [5] do not rule out some participation of carbonyl groups in CT complex formation for arenetricarbonylchromium molecules wherein the acceptor interaction with the aromatic ring is sterically hindered. In most cases coordination of the TNB molecule with arenetricarbonylchromium proceeds with the aromatic ring with resulting formation of a π,π-type molecular complex. The increase of the charge-transfer energy in the course of introduction of electron-withdrawing groups onto the ring (favoured by the presence of the electron-withdrawing group Cr(CO)$_3$) is a characteristic feature of CT complexes of the π,π-type, which is supported quantitatively by the presence of a linear correlation between ν(CT) of molecular complexes of the compounds studied with TNB (Table 1) and σ_p^+-constants in the benzene ring (Fig. 1).

$$\nu(\mathrm{CT}) = 1060\ \Sigma\sigma_p^+ + 20700 \qquad (r = 0.87)$$

It will be noted that the CT energy variation in complexes with TNB in the course of transition from arenetricarbonylchromium complexes 3 to 17 (Table 1) occurs to a far lesser extent than the corresponding variation for

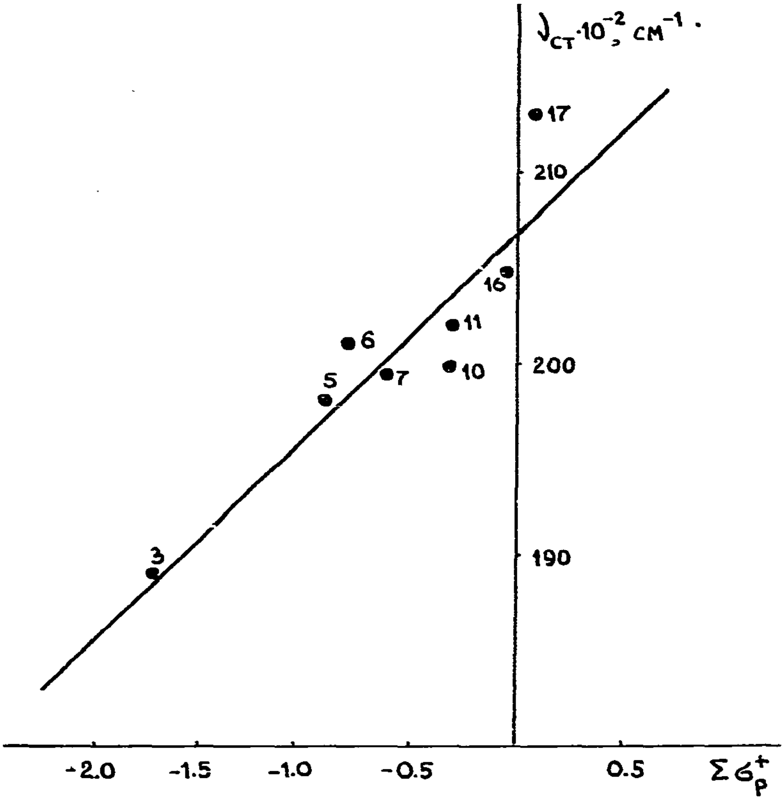

Fig. 1. Charge-transfer frequency (ν(CT)) versus the sum of Brown-Okamoto (σ_p^+) substituent constants in benzene ring of the compounds studied (CT complexes with TNB).

the arenes 3—17 in CT complexes with TCNE ($\Delta\nu$(TNB) = 2700 cm^{-1} versus $\Delta\nu$(TCNE-ARENE) = 10500 cm^{-1}).

Consistent with the low electron affinity values of the TNB molecule, the CT complexes studied are rather weak, as can be seen both from their equilibrium constant values [6] and from the low values of the correlation coefficient of the relationship quoted above.

Let us proceed to consideration of the charge-transfer complexes of arenetricarbonylchromium with TCNE studied (Table 1). As can be seen from Table 1, in contrast to CT complexes of arenes with TCNE and CT arenetricarbonylchromium complexes with TCNE, on increasing the σ_p^+-constants of substituents on the benzenetricarbonylchromium ring, the CT energy (ν(CT)) decreases. The CT energy in such molecular complexes is much less dependant on substituent effects than in the corresponding uncoordinated arenes ($\Delta\nu$(TCNE-ATCC) = 3900 cm^{-1} and $\Delta\nu$(TCNE-ARENE) = 10500 cm^{-1} in the course of transition from compound 3 to 17. In addition, the CT band in electronic absorption spectra of arenetricarbonylchromium complexes with TCNE is located at a longer wavelength compared with that of complexes of

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* ATCC = arenetricarbonylchromium.

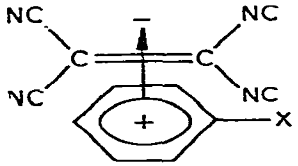
the corresponding compounds with TNB. This may be accounted for by stronger bonding in the CT complexes with TCNE (electron affinity E_A of TCNE equals 1.8 versus 0.7 for TNB; equilibrium constants of CT complex formation with TCNE are one or two orders higher than corresponding values of CT complexes with TNB [6]. It is less obvious, considering the presence of the strong electron withdrawing group $Cr(CO)_3$ in the arenetricarbonylchromium molecules, what the reason is for the remarkable bathochromic shift of the CT band of CT complexes with TCNE compared with the corresponding band for uncoordinated arenes.

Thus, if CT arenetricarbonylchromium complexes with TCNE are supposed to be of the π,π-type (which is quite reasonable as a characteristic π-acceptor, tetracyanoethylene, coordinates with an aromatic π-system on the principle of maximum overlap [11]) the data observed seem to contradict one of the main features of such complexes, namely, that the introduction of an electron-withdrawing substituent must result in increase rather than in decrease of the CT frequency. This observation made it possible for Kobayashi et al. [6,7] to advance the hypothesis that tetracyanoethylene in molecular complexes with arenetricarbonylchromium interacts direct with the chromium atom and in molecular complexes with arenetricarbonyl-molybdenum and -tungsten it coordinates with the corresponding metal atoms. Their assumptions were based furthermore on the IR data (consideration of the stretching mode of the CO bond) and on semiempirical calculations of MO energy.

Indeed, as follows from the experimental data (in particular from the characteristic features of the electronic absorption spectra mentioned above) as well as from comparison of ionization potential values of arenetricarbonylchromium, arene and free metal [5] and also from MO calculations [6,7] the highest occupied molecular orbital (HOMO) of the complexes studied is of mixed π-character (aromatic ligand), d-character (central metal atom) and σ-character (metal—carbonyl group bond). Nevertheless it is not necessary to make use of the hypothesis concerning coordination of TCNE with the metal atom to explain the anomalous character of CT energy dependance on the electronic properties of substituents in the ring.

The alternative explanation may be as follows.

In the course of CT-complex formation (for example of π,π-type) a partial transfer of electron density from the aromatic donor to the π-acceptor (for example TCNE) takes place. As a result a positive charge forms on the ring, with a value depending, as it known, on the donor ionization potential and on the acceptor electron affinity and likewise upon the donor-acceptor properties



of the substituent X. When X is a electron withdrawing group, the positive charge value on the ring increases in comparison with the case when X is a electron donor. Such alteration of substituent-ring conjugation is represented in terms of correlation analysis by a linear relationship between ν(CT) and σ_p^+-constants of substituents in the ring [17]. In the case of arenetricarbonylchromium, the presence of the positive charge on the ring leads to an alteration of the degree of conjugation with the ring not only of substituents X but of the group $Cr(CO)_3$ as well. It follows that the group $Cr(CO)_3$, along with the electron withdrawing features mentioned above, in the presence of a strongly electron deficient center on the benzene ring may act as the electron donor. This strongly electron deficient center forms in the excited state of the CT complex with TCNE ($E_A = 1.8$).

It is known [12], that the degree of the back donation of the electron density from chromium towards the π-ligand (aromatic ring) depends upon the nature of the other ligands (in the present case it depends on the nature of substituents on the ring). The value of the positive charge on the aromatic ring of arenetricarbonylchromium, in the case of CT complex formation with the strong π-acceptor (TCNE), increases with an increase of electron-withdrawing properties of substituents on the ring. Simultaneously the donation of electron density also increases from the tricarbonylchromium group towards the ring (note, that such a donation is not excluded in theoretical consideration of this work [7]) and the CT band shifts to longer wavelength. In fact we deal simultaneously with two electron donation processes, i.e. intramolecular (chromium atom—aromatic ligand), studied earlier by electronic absorption spectroscopy of arenetricarbonylchromium compounds [18] and intermolecular (arenetricarbonylchromium—TCNE).

As it was assumed that the TCNE interacts with the π-coordinated benzene ring, one may expect that the influence of substituents on the ring on the CT band position is given by conjugation mechanism, similar to that for ordinary benzene derivatives. This polar effect of substituents should be depicted, as mentioned above, by their σ_p^+-constants. Accordingly we established a linear relationship between the position of the CT band (ν(CT)) in the electronic absorption spectra of CT arenetricarbonylchromium with TCNE and the values of σ_p^+-constants of substituents in the aromatic ring, expressed by the following relationship (see Fig. 2):

$$\nu(\mathrm{CT}) = 13300 - 1550\ \Sigma\sigma_p^+ \qquad (r = 0.95)$$

In the case of TCNE coordination with chromium, the substituent effect in the ring on the ν(CT) value would be inductive [12]. Nevertheless, the attempt to establish the relationship between ν(CT) and the sum of inductive constants (σ^*) reveals inadequate correlation between those values.

From the considerations quoted above we propose that tetracyanoethylene interacts with the aromatic ring of the arenetricarbonylchromium derivatives. With a view to further consideration of this problem we have studied the electronic spectra of CT complexes of some compounds with π-acceptors intermediate between TNB and TCNE in their electron affinity value E_A (Table 1). Fig. 3 shows the dependence of charge-transfer (ν(CT)) frequency in the electronic absorption spectra of CT complexes of arenetricarbonylchromium derivatives (for a discussion of the point positions corresponding to molybdenum and tungsten derivatives see below) upon affinity value for electron acceptors. On

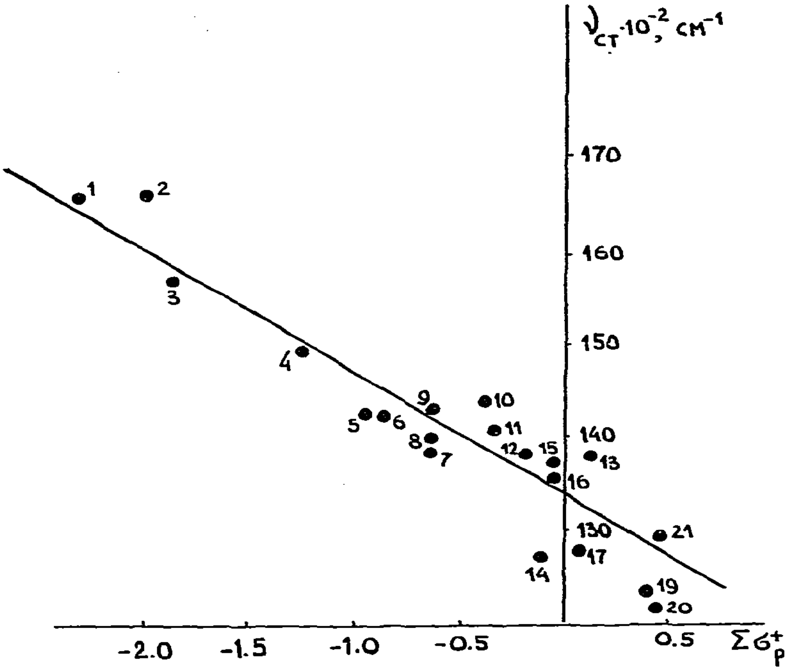


Fig. 2. Charge-transfer frequency (ν(CT)) versus the sum of Brown-Okamoto (σ_p^+) substituent constants in benzene ring of the compounds studied (CT complexes with TCNE).

the basis of this relationship one may draw the following conclusions.

As it was already noted, the value of the positive charge on the ring appearing in the course of excitation of the CT complex depends on the donor ionization potential and the electron affinity of the acceptor, this value being determined first of all by the E_A acceptor value for the same donor (e.g. compound 3, Table 1). The variation of the positive charge value on the ring results in alteration of the donor—acceptor interaction of the $Cr(CO)_3$ fragment with the arene. In accordance with that it is possible to single out three regions in the Fig. 3:

(1) $E_A < 0.8$; (2) $0.7 < E_A < 1.7$; (3) $E_A > 1.7$

The side regions respond to formation of CT complexes with the TNB π-acceptor (region 1), and with the relatively strong TCNE (region 3).

Both cases are discussed in details above. We emphasize once more that in case 1, a small positive charge appearing on the ring is compensated by the influence of substituent X in the ring; the $Cr(CO)_3$ group electron density is not effected and it plays the role of an electron acceptor. In case 3 the positive charge on the ring is high enough for the tricarbonylchromium group to exhibit electron donor properties. The sensitivity of the CT energy to substituents influence in the ring in this case is higher than in the case 1.

In the intermediate case 2, the CT band frequency does not depend on the σ_p^+-constant values of substituents in the aromatic ligand of the arenetricarbonylchromium complex. This may be accounted for by the $Cr(CO)_3$ fragment being very sensitive to all electron density changes on the aromatic ring and the tricar-

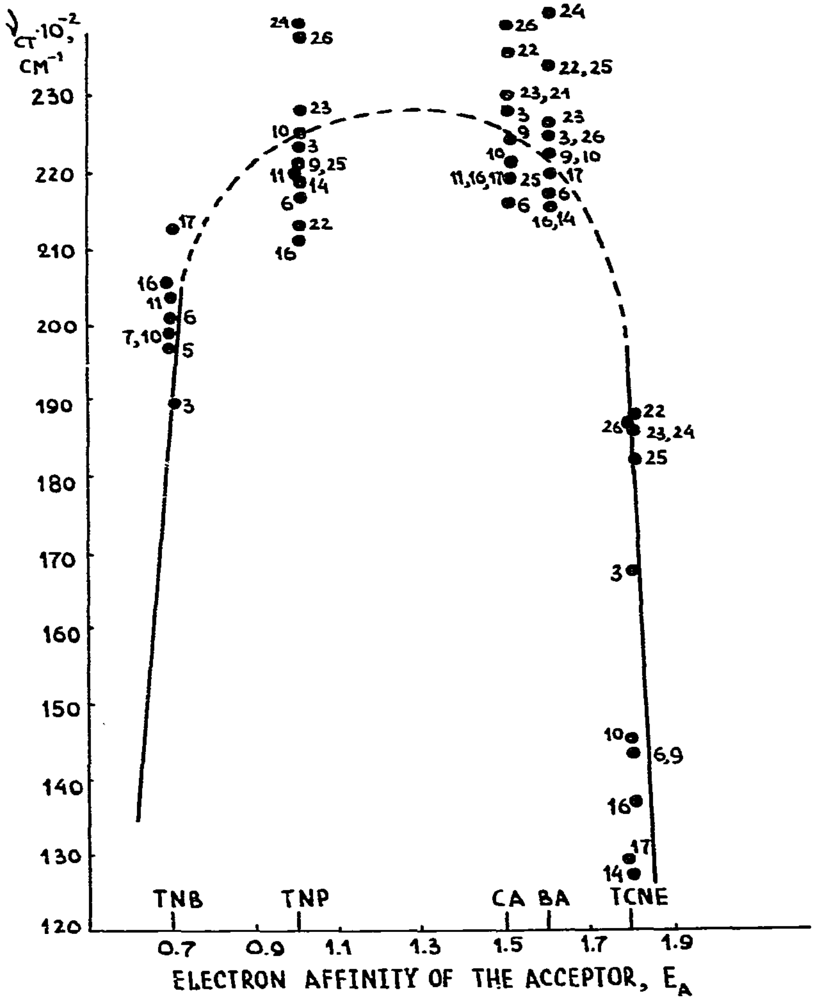


Fig. 3. The values of ν(CT) for CT complexes of the compounds studied versus electron affinity of some π-acceptors.

bonylchromium group compensating to a substantial degree electronic effects of substituents X in the ring. It is noteworthy that in the course of the transition from TNB to TNP the change in ν(CT) occurs as an effect of electron donating and in the course of the transition from TCNE to BA and CA as an effect of the electron withdrawing properties of the $Cr(CO)_3$ group. The variation of E_A values in the range 1—1.5 would make it possible to bring out more clearly the maximum of the dashed curve, this is the region where the compensation mentioned is practically complete. Thus the assumption of coordination of all π-acceptors, including tetracyanoethylene with aromatic ligand appears to satisfactory account for the donor—acceptor properties of arenetricarbonylchromium.

Let us consider briefly the electronic effects in arenetricarbonylmolybdenum and arenetricarbonyltungsten (Table 2, Fig. 3). Charge-transfer complexes of

TABLE 2

CHARGE TRANSFER FREQUENCIES (ν(CT)) IN SPECTRA OF CT ARENETRICARBONYLMOLYBDENUM AND TUNGSTEN COMPLEXES WITH VARIOUS ACCEPTORS

Number	compound	charge transfer frequency ν(CT) × 10^{-2} (cm^{-1})					$\Sigma\sigma_p^+$
		TCNE	BA	CA	TNP	TNB	
22	$(CH_3)_2C_6H_4Mo(CO)_3$	187	234	236	213		—0.6
23	$C_2H_5C_6H_5Mo(CO)_3$	185	226	230	228		—0.31
24	$CH_3C_6H_5Mo(CO)_3$	185 [a]	241	230	239		—0.31
25	$C_2H_5C_6H_5W(CO)_3$	182	234	220	221		—0.31
26	$CH_3C_6H_5W(CO)_3$	186	225	239	238		—0.31

[a] Ref. 6 data.

these compounds with TNB were not identified by electronic absorption spectroscopy. The CT bands corresponding to molybdenum and tungsten complexes with TCNE reveal a pronounced gypsochromic shift compared with similar CT arenetricarbonyl complexes. The energy sensitivity of CT in the studied TCNE complexes of molybdenum and tungsten to the substituent effects in the ring and to the central metal atom substitution is extremely low, which correlates well with the literature data [7] (in particular it was shown by photoelectronic spectroscopy that ionization potentials of Mo and W complexes are practically the same, but they substantially exceed ionization potentials of corresponding chromium complexes). If we will start again from the assumption that the coordination of the TCNE molecule in CT arenetricarbonyl-molybdenum- and -tungsten complexes proceeds to the aromatic ring, then the mentioned pecularities of compounds from Table 2 may be explained to be as a result of a substantial increase of the electron withdrawing properties of the $Mo(CO)_3$ and $W(CO)_3$ fragments compared with that of $Cr(CO)_3$. From the electronic spectroscopy data of CT complexes this sequence is Cr < Mo ≈ W, and from IR spectroscopy data (the shift of C—O stretching mode) [7] the series Cr < Mo < W is observed. The strong electron withdrawing properties of molybdenum- and tungsten-tricarbonyl groups impede CT complex formation with such a weak π-acceptor as TNB, at the same time the same tendency in CT energy change is observed for CT-complexes with TNB, namely, decrease in values of σ_p^+-constants of substituents in the ring leads to the decrease of ν(CT) value. The relation of ν(CT) in CT complexes of the compounds studied with BA and XA is not regular and the further gypsochromic shift of the CT band is observed as in the case of CT complexes with TNP (the points in the upper region in the Fig. 2).

In conclusion it is interesting to note the following fact. It is known [19] that the basicity of the central metal atom in arenetricarbonylmetal increases in the series Cr < Mo << W, that is why the tendency of the π-acceptor (e.g. TCNE) to coordinate on the central metal atom should increase in the same sequence. However, comparison of the data from Tables 1 and 2 favours just an opposite relation and that also may serve as a confirmation of our assumption concerning the location of π-acceptor coordination.

Experimental

The electronic absorption spectra of CT complexes were measured on a Perkin-Elmer-402 spectrophotometer in the 300—850 nm region. The solution of the compounds studied in CH_2Cl_2 ($\sim 10^{-2}$ mole l^{-1}) BA and CA ($\sim 5 \times 10^{-3}$ mole l^{-1}), TNB and TNP ($\sim 10^{-2}$ mole l^{-1}) were mixed 5 : 1 in volume to record the spectra. The concentration of acceptor solutions was one or two orders less when the spectra of CT arenetricarbonyl-molybdenum and -tungsten complexes were measured. The cell path was 2 cm.

The compounds investigated were prepared using the methods previously described [13].

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