

Charge-Transfer Complexes of Some Metal 2,4-Pentanedionates with Picric Acid as π -Acceptor

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요 약. 2,4-펜탄디온 금속 화합물과 피크릭산과 같은 π -오비탈 전자 받계의 반응에 의해 전하 전달 화합물을 합성 하였고 특성들에 대하여 연구하였다. 상온하의 클로로포름에서 화합물들의 분광학적 특성과 안정성이 전자 주계 분자 구조와 π -오비탈 전자 받계의 관점 하에서 조사하고 논의하였다. 실험 결과로는 $[M(acac)_n(PA)]$ ($M=Cu(II), Ni(II), Mn(II), Fe(III), Co(III), Cr(III), Al(III), Zr(IV); n=2, 3, 4; PA=picric acid$)와 같은 일반적인 화학식을 가진 전하 전달 화합물 들이 생성됨을 나타내었다. 전하 전달 흡수, 원소 분석, IR 분광 스펙트럼, 중량 측정 연구들에 대하여 토의하였다.

주제어: 전하전달, 2,4-펜탄디온 화합물, π -오비탈 전자 받계, 피크릭산

ABSTRACT. The charge-transfer complexes formed between some different metal 2,4-pentadionato complexes and π -electron acceptor (picric acid, PA) are synthesized and characterized. Spectral characteristics and stability of the complexes are investigated and discussed in terms of donor molecular structure and π -acceptor at room temperature in chloroform. The results indicate the formation of 1:1 charge-transfer complexes with a general formula, $[M(acac)_n(PA)]$ where ($M=Cu(II), Ni(II), Mn(II), Fe(III), Co(III), Cr(III), Al(III)$ and $Zr(IV); n=2, 3$ or 4). The charge-transfer absorptions, elemental analysis, infrared spectra and gravimetric studies were recorded and discussed.

Keywords: Charge-Transfer, 2,4-Pentanedionato Complexes, π -Acceptors, Picric Acid

INTRODUCTION

One interesting aspect of the chemistry of metal acetylacetonates $[M(acac)_n]$ concerns the pseudo aromatic π -electron delocalization in the $[M(acac)_n]$ rings.¹ The ability of $[M(acac)_n]$ compounds to form molecular complexes with σ -acceptor I_2 ,²⁻⁸ is one property that has been taken as evidence for such delocalization.¹ It was proposed that these complexes are similar to those formed by aromatic hydrocarbons with I_2 and that $[M(acac)_n]$ compounds

behave as π -electron donors.

Recently, we have reported the formation of new CT-complexes formed from the reaction of ferric(III) acetylacetonate, $Fe(acac)_3$, with different types of σ (iodine) and π -electron acceptors (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) (DDQ), tetrachloro-*p*-benzoquinone (*p*-chloranil) and 7,7',8,8'-tetracyanoquinodimethane (TCNQ)).⁸

In the last few years, chemical and physical properties of some charge transfer complexes formed by the reaction of π -electron acceptors with some het-

erocyclic amines have been the subject of many investigations.⁹⁻¹¹ some of these charge-transfer complexes show very interesting applications in the analysis of some drug in pure form or in pharmaceutical preparations^{12,13} and some of the CT-complexes show very interesting physical properties such as electrical conductivity.^{14,16}

To continue these reports in this area,^{7,8} present investigation deals with the formation of the new CT-complexes obtained in the reaction of different metal acetylacetonates [Cu(II), Ni(II), Mn(II), Fe(III), Co(III), Cr(III), Al(III) and Zr(IV)] with picric acid (PA). All reactions were carried out in chloroform as a solvent. The obtained results lead to investigate the rapture of bonding and structure inherent in these new complexes.

EXPERIMENTAL

All chemicals used in this study were of high pure grade and used without further purification. Different metal acetylacetonates (Cu(II), Ni(II), Mn(II), Fe(III), Co(III), Cr(III), Al(III) and Zr(IV)) were obtained from Merck Chemical Co., while picric acid (PA) was purchased from BDH.

The solid donor-acceptor complexes were isolated as follows. Excess saturated solution of the acceptor (picric acid, PA) in chloroform (40 ml) was added to a saturated solution for each of the donors (10 ml) in chloroform. The mixture in each case was stirred for about 10-15 min. The CT-solid complexes formed were filtered immediately and washed several times with minimum amounts of chloroform (3-5 ml) and dried under vacuum.

The formed complexes were characterized by their elemental analysis, vibrational and electronic absorption spectroscopy. The analysis data were shown in Table 1. Copper(II), nickel(II), manganese(II), ferric(III), cobalt(III), chromium(III), aluminum(III) and zirconium(IV) contents in all charge-transfer complexes were determined gravimetrically as a stable metal oxide.

Absorption spectra of the donors [Cu(acac)₂], [Ni(acac)₂], [Mn(acac)₂], [Fe(acac)₃], [Co(acac)₃], [Cr(acac)₃], [Al(acac)₃] or [Zr(acac)₄], acceptor (picric

acid (PA)) and the formed CT-complexes in chloroform were scanned in the region of 700-200 nm using a Shimadzu UV-spectrophotometer model 1601 PC using 1 cm matched quartz cell. The mid infrared spectra of the reactants and the formed CT-complexes were recorded from KBr discs using a Genesis II FT-IR. Photometric titration were performed¹⁷ at 25 °C for the reactions of different acetylacetonates with the acceptor (PA) in chloroform as follow. The concentrations of all donors [Cu(acac)₂], [Ni(acac)₂], [Mn(acac)₂], [Fe(acac)₃], [Co(acac)₃], [Cr(acac)₃], [Al(acac)₃] and [Zr(acac)₄] in the reaction mixtures were kept fixed at (1.0×10⁻⁵ M), while the concentration of acceptor picric acid was changed over the range from 0.25×10⁻⁵ to 3.00×10⁻⁵ and these produced solutions with donor : acceptor ratios varying from 1 : 0.25 to 1 : 3, as shown in Table 2.

RESULTS AND DISCUSSION

The ultraviolet-visible absorption spectra of the reactants, metal acetylacetonates (M=Cu(II), Ni(II), Mn(II), Fe(III), Co(III), Cr(III), Al(III) and Zr(IV)), (0.2×10⁻⁴ M) and π-acceptor (PA=picric acid) (0.2×10⁻⁴ M) in CHCl₃ along with those of the obtained 1:1 CT-complexes are shown in Fig. 1 (A-H, respectively). The spectra demonstrate that the formed CT-complexes have strong absorption bands around 321 and 420 nm for [Cu(acac)₂(PA)]; 387, 411 and 495 nm for [Ni(acac)₂(PA)]; 324, 376 and 407 nm for [Mn(acac)₂(PA)]; 345, 405 and 483 nm for [Fe(acac)₃(PA)]; 319, 369 and 450 nm for [Co(acac)₃(PA)]; 361 and 424 nm for [Co(acac)₃(PA)]; 358 and 423 nm for [Al(acac)₃(PA)]; 360 and 440 nm for [Zr(acac)₄(PA)]. complexes. These bands do not exist in the spectra of the reactants. The stoichiometry of the [M(acac)_n]-PA (n=2 for M=Cu, Ni and Mn, n=3 for M=Fe, Co, Al and Cr, n=4 for M=Zr(IV)) reactions was shown in all cases to be of ratio 1 : 1. This was interpreted on the bases of the obtained elemental analysis data of the isolated solid CT-complexes as indicated in the experimental section, gravimetric measurements by calculated the weight loss and the final thermal products as metal oxides

Table 1. Elemental analysis data and gravimetric measurements for $[M(\text{acac})_3(\text{PA})]$

Complexes	M. Wt.	%C		%H		%N		%M		Gravimetric analysis				
										Total weight loss		Total residue		Final product
		Calc	Found	Calc	Found	Calc	Found	Calc	Found	Calc	Found	Calc	Found	
$[\text{Cu}(\text{acac})_3(\text{PA})]$	490.87	39.11	38.77	3.46	3.42	8.55	8.47	12.95	13.44	83.79	83.18	16.21	16.82	CuO
$[\text{Ni}(\text{acac})_3(\text{PA})]$	486.02	39.50	39.12	3.49	3.38	8.64	8.56	12.08	12.17	84.63	84.51	15.37	15.49	NiO
$[\text{Mn}(\text{acac})_3(\text{PA})]$	480.38	39.97	39.45	3.54	3.50	8.74	8.70	11.44	11.53	81.90	81.75	18.10	18.25	MnO ₂
$[\text{Fe}(\text{acac})_3(\text{PA})]$	582.29	43.28	43.11	4.12	4.07	7.21	7.14	9.59	9.67	86.29	86.17	13.71	13.83	Fe ₂ O ₃
$[\text{Co}(\text{acac})_3(\text{PA})]$	585.37	43.05	42.89	4.10	4.06	7.17	7.09	10.07	10.14	85.83	85.73	14.17	14.27	Co ₂ O ₃
$[\text{Cr}(\text{acac})_3(\text{PA})]$	578.44	43.56	43.37	4.15	4.11	7.26	7.21	8.99	9.11	86.86	86.69	13.14	13.31	Cr ₂ O ₃
$[\text{Al}(\text{acac})_3(\text{PA})]$	553.42	45.53	45.24	4.34	4.33	7.59	7.36	4.87	5.05	90.79	90.46	9.21	9.54	Al ₂ O ₃
$[\text{Zr}(\text{acac})_3(\text{PA})]$	716.77	43.53	43.41	4.32	4.26	5.86	5.84	12.72	12.76	82.81	82.76	17.19	17.24	ZrO ₂

Table 2. The electronic absorption spectral data for $[M(\text{acac})_3(\text{PA})]$ (where $n=2$ for M-Cu(II), Ni(II), Mn(II); $n=3$ for M-Fe(III), Co(III), Cr(III), Al(III); $n=4$ for M-Zr(IV)) complexes in CHCl₃

X ml of PA	D:A ratio	Absorbance															
		$[\text{Cu}(\text{acac})_3(\text{PA})]$		$[\text{Ni}(\text{acac})_3(\text{PA})]$		$[\text{Mn}(\text{acac})_3(\text{PA})]$		$[\text{Fe}(\text{acac})_3(\text{PA})]$		$[\text{Co}(\text{acac})_3(\text{PA})]$		$[\text{Cr}(\text{acac})_3(\text{PA})]$		$[\text{Al}(\text{acac})_3(\text{PA})]$		$[\text{Zr}(\text{acac})_3(\text{PA})]$	
		321 nm	420 nm	387 nm	495 nm	324 nm	407 nm	345 nm	483 nm	319 nm	450 nm	361 nm	424 nm	358 nm	423 nm	360 nm	440 nm
0.25	1:0.25	0.540	0.154	0.521	0.185	0.568	0.122	0.825	0.150	0.648	0.075	0.403	0.063	0.175	0.089	0.227	0.096
0.50	1:0.50	1.050	0.269	0.948	0.357	1.021	0.208	1.325	0.278	1.125	0.133	0.850	0.119	0.318	0.168	0.398	0.182
0.75	1:0.75	1.562	0.361	1.396	0.507	1.503	0.303	2.025	0.398	1.675	0.175	1.425	0.173	0.456	0.250	0.599	0.261
1.00	1:1.00	2.175	0.450	1.706	0.741	2.007	0.381	2.787	0.493	2.275	0.222	1.825	0.223	0.612	0.308	0.727	0.334
1.50	1:1.50	2.550	0.556	2.175	0.875	2.483	0.538	3.198	0.675	2.746	0.295	2.125	0.315	0.712	0.425	0.892	0.450
2.00	1:2.00	2.848	0.645	2.667	1.075	2.921	0.653	3.548	0.799	3.125	0.333	2.453	0.402	0.825	0.518	1.042	0.549
2.50	1:2.50	3.175	0.725	3.025	1.275	3.294	0.758	3.978	0.848	3.575	0.385	2.875	0.476	0.937	0.612	1.229	0.629
3.00	1:3.00	3.525	0.775	3.375	1.435	3.660	0.857	4.375	0.991	4.075	0.413	3.199	0.453	1.068	0.706	1.371	0.724

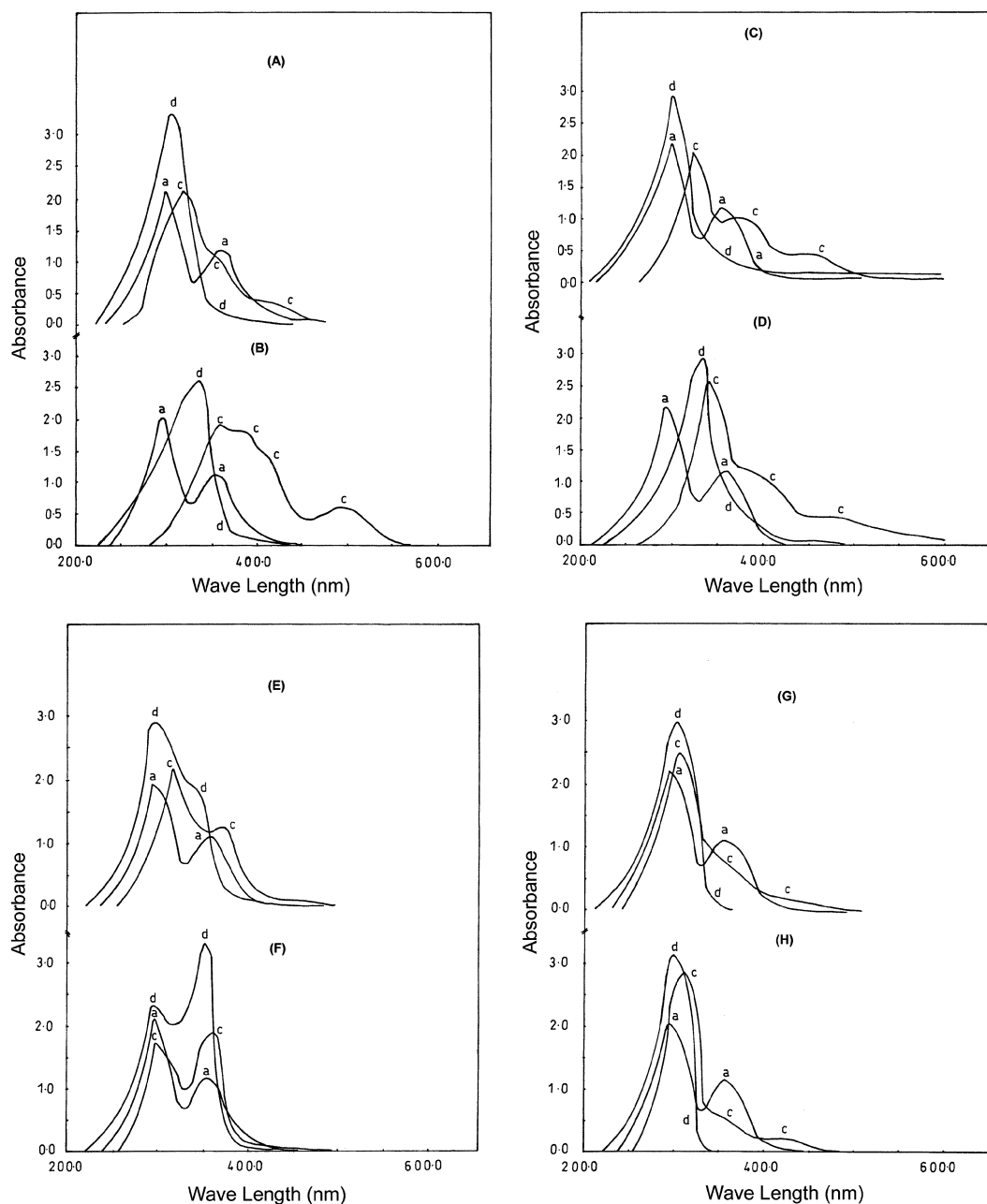


Fig. 1. Electronic absorption spectra of (A): $[\text{Cu}(\text{acac})_2]$ -PA reaction in CHCl_3 ; (B): $[\text{Ni}(\text{acac})_2]$ -PA reaction in CHCl_3 ; (C): $[\text{Mn}(\text{acac})_3]$ -PA reaction in CHCl_3 ; (D): $[\text{Fe}(\text{acac})_3]$ PA reaction in CHCl_3 ; (E): $[\text{Co}(\text{acac})_3]$ -PA reaction in CHCl_3 ; (F): $[\text{Cr}(\text{acac})_3]$ -PA reaction in CHCl_3 ; (G): $[\text{Al}(\text{acac})_3]$ PA reaction in CHCl_3 ; (H): $[\text{Zr}(\text{acac})_4]$ PA reaction in CHCl_3 . (a) =acceptor ($0.2 \cdot 10^{-4} \text{ M}$), (d)=donor ($0.2 \cdot 10^{-4} \text{ M}$) and (c)= donor-acceptor CT-complex.

for all CT-complexes, as well as from the complexes infrared spectra, which indicate the existence of the bands characteristic for both the

$[\text{M}(\text{acac})_n]$ and the picric acid as π -acceptor. The stoichiometry of 1 : 1 is also strongly supported by photometric titration measurements. These mea-

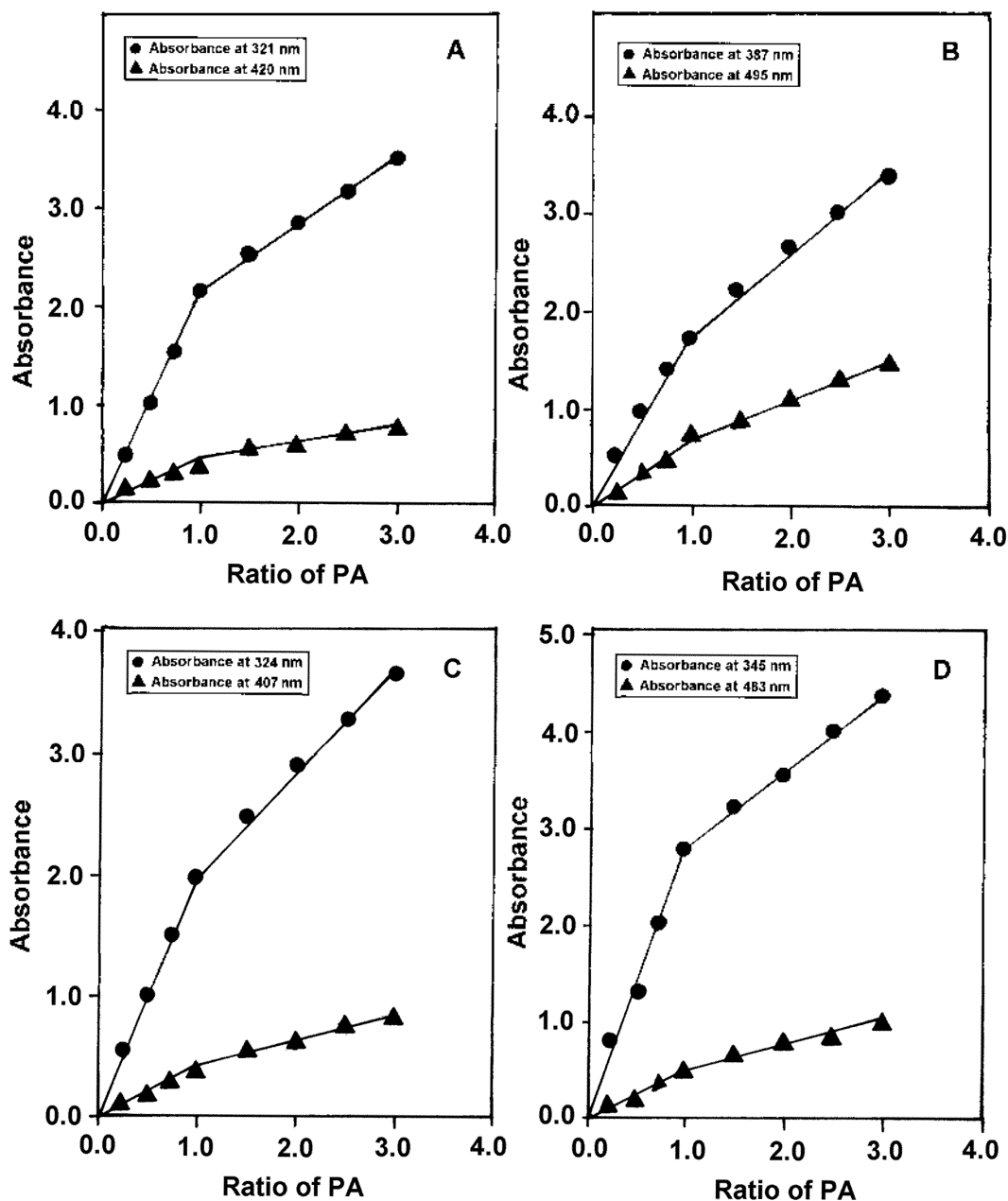


Fig. 2. Photometric titration curves for the $[M(acac)_3]$ -PA reactions in $CHCl_3$: (A): $[Cu(acac)_3]$ -PA, (B): $[Ni(acac)_3]$ -PA, (C): $[Mn(acac)_3]$ -PA, (D): $[Fe(acac)_3]$ -PA, (E): $[Co(acac)_3]$ -PA, (F): $[Cr(acac)_3]$ -PA, (G): $[Al(acac)_3]$ -PA, (H): $[Zr(acac)_3]$ -PA.

measurements were based on strong absorption bands at 321 and 420 nm for $[Cu(acac)_3]$ -PA; at 387, 411 and 495 nm for $[Ni(acac)_3]$ -PA; at 324, 376 and 407 nm for $[Mn(acac)_3]$ -PA; at 345, 405 nm and 483 nm for $[Fe(acac)_3]$ -PA; at 319, 369 and 450 nm for $[Co(acac)_3]$ -

PA; at 361 and 424 nm for $[Cr(acac)_3]$ -PA; at 358 and 423 nm for $[Al(acac)_3]$ -PA and at 360 and 440 nm for $[Zr(acac)_3]$ -PA, see Table 2.

In these measurements, concentration of $[M(acac)_3]$ was kept fixed, while the concentration of the accep-

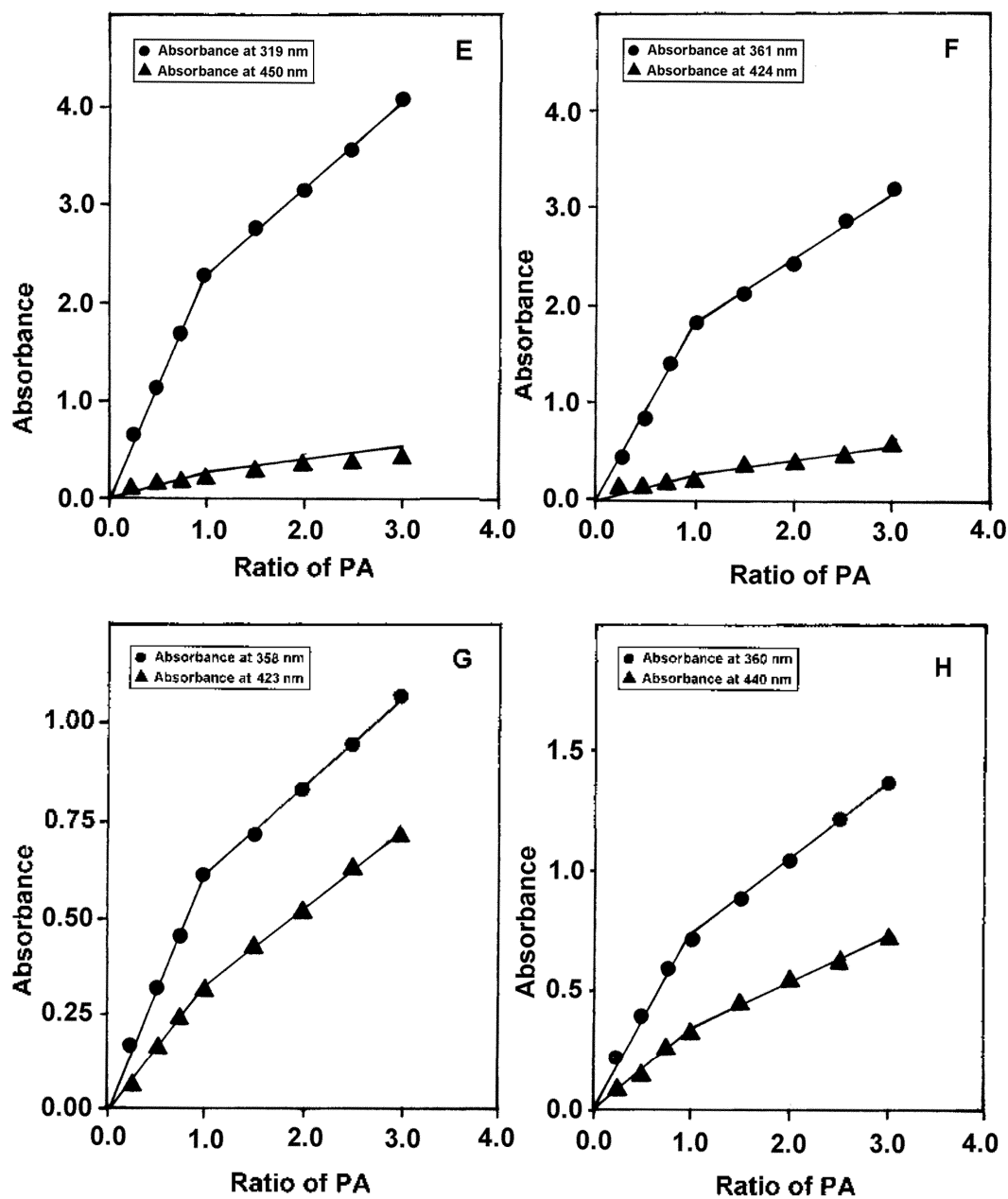


Fig. 2. (Continued)

tor (PA) was varied over the range of 0.25×10^{-5} M to 3.00×10^{-5} M as described in the experimental section. Photometric titration curves based on these measurements are shown in Fig. 2(A-H). The $[M(acac)_n]$ -acceptor equivalence points indicate that the $[M(acac)_n]$: acceptor ratio in all cases is 1 : 1,

and this result agrees quite well with the elemental analysis, and infrared spectra of the solid CT-complexes. Accordingly, the formed CT-complexes upon the reaction of $[M(acac)_n]$ as a donor with the π -acceptor picric acid (PA) under investigation in chloroform have the general formula $[M(acac)_n(PA)]$.

Table 3. The values C_a^o , C_d^o , C_a^o/C_d^o , $C_a^o C_d^o$ and $C_a^o C_d^o$ for $[M(acac)_n(PA)]$ (where $n=2$ for M–Cu(II), Ni(II), Mn(II); $n=3$ for M–Fe(III), Co(III), Cr(III), Al(III); $n=4$ for M–Zr(IV)) complexes in $CHCl_3$

D:A ratio	$C_a^o \cdot 10^5$	$C_d^o \cdot 10^5$	$(C_a^o/C_d^o) \cdot 10^{-7}$	$(C_a^o C_d^o) \cdot 10^{-10}$	$(C_a^o C_d^o) \lambda \cdot 10^{-10}$															
					[Cu(acac) ₂ (PA)]		[Ni(acac) ₂ (PA)]		[Mn(acac) ₂ (PA)]		[Fe(acac) ₃ (PA)]		[Co(acac) ₃ (PA)]		[Cr(acac) ₃ (PA)]		[Al(acac) ₃ (PA)]		[Zr(acac) ₄ (PA)]	
					321 nm	420 nm	387 nm	495 nm	324 nm	407 nm	345 nm	483 nm	319 nm	450 nm	361 nm	424 nm	358 nm	423 nm	360 nm	440 nm
1: 0.25	1.00	0.25	125	0.25	0.463	1.623	0.479	1.347	0.441	2.049	0.303	1.667	0.385	3.333	0.620	3.989	1.428	2.797	1.103	2.604
1: 0.50	1.00	0.50	150	0.50	0.476	1.861	0.527	1.399	0.489	2.403	0.377	1.797	0.444	3.748	0.588	4.175	1.572	2.976	1.256	2.699
1: 0.75	1.00	0.75	175	0.75	0.480	2.085	0.537	1.480	0.507	2.503	0.378	1.884	0.448	4.285	0.526	4.335	1.644	3.000	1.257	2.875
1: 1.00	1.00	1.00	200	1.00	0.459	2.222	0.586	1.352	0.508	2.624	0.358	2.028	0.439	4.497	0.548	4.475	1.634	3.250	1.375	2.994
1: 1.50	1.00	1.50	250	1.50	0.588	2.697	0.690	1.714	0.604	2.788	0.469	2.222	0.546	5.085	0.706	4.748	2.107	3.529	1.682	3.333
1: 2.00	1.00	2.00	300	2.00	0.702	3.109	0.749	1.860	0.685	3.058	0.564	2.503	0.640	5.995	0.815	4.975	2.424	3.861	1.919	3.643
1: 2.50	1.00	2.50	350	2.50	0.787	3.448	0.826	1.961	0.759	3.298	0.629	2.948	0.699	6.501	0.869	5.250	2.668	4.085	2.034	3.974
1: 3.00	1.00	3.00	400	3.00	0.851	3.871	0.889	2.094	0.819	3.504	0.685	3.027	0.736	7.253	0.938	5.525	2.808	4.249	2.188	4.144

The 1:1 modified Benesi-Hildebrand equation¹⁸ was used in calculating the values of the equilibrium constant K (l mol^{-1}) and the extinction coefficient, ϵ ($\text{l mol}^{-1} \text{cm}^{-1}$).

$$\frac{C_a^0 C_d^0 L}{A} = \frac{1}{K\epsilon} + \frac{C_a^0 - C_d^0}{\epsilon}$$

C_a^0 and C_d^0 are the initial concentrations of the

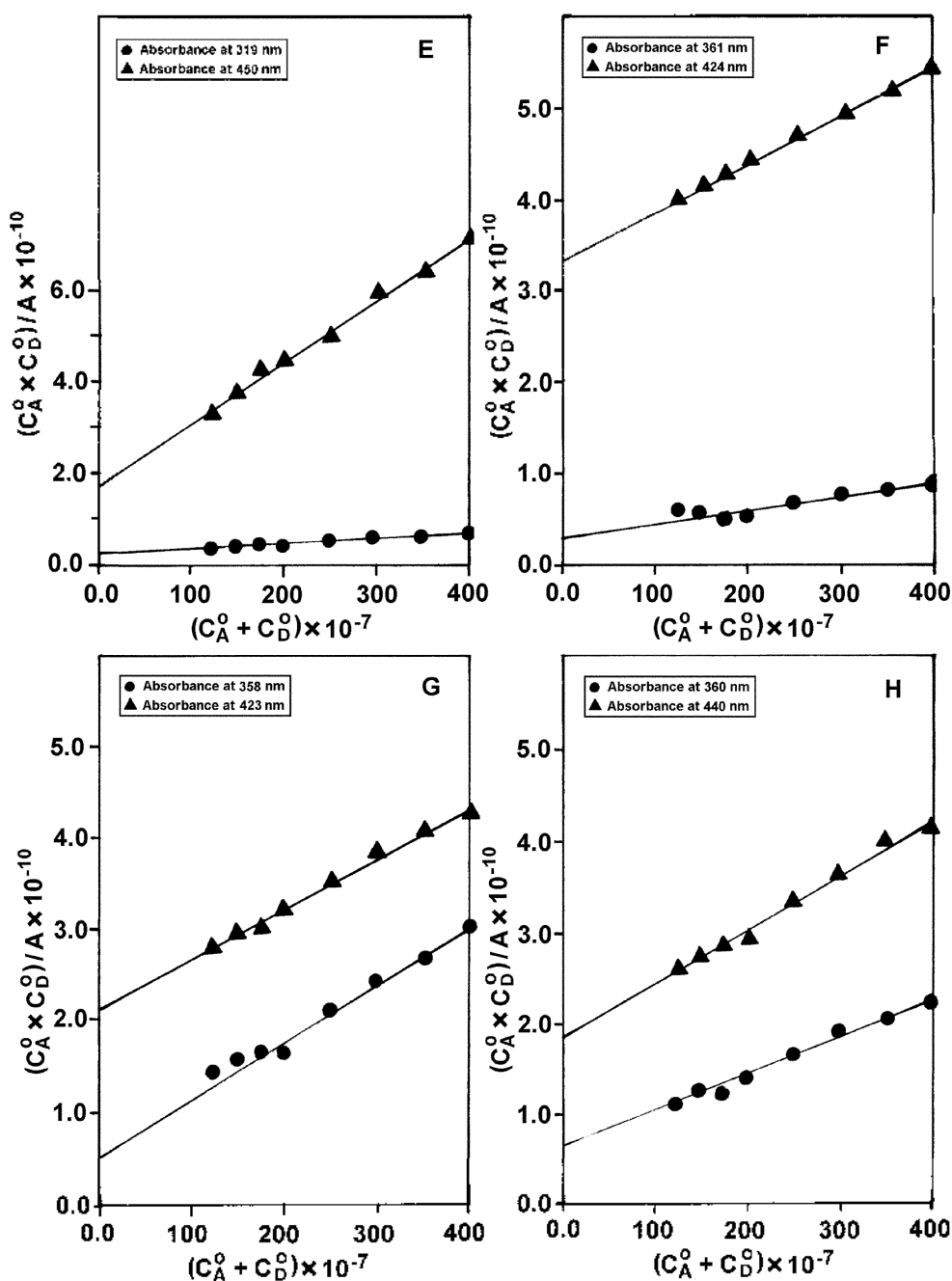


Fig. 3. The plot of $(C_A^0 \cdot C_D^0) / A$ values against $(C_A^0 + C_D^0)$ values for the reaction of: (A): $[\text{Cu}(\text{acac})_2]$ -PA, (B): $[\text{Ni}(\text{acac})_2]$ -PA, (C): $[\text{Mn}(\text{acac})_2]$ -PA, (D): $[\text{Fe}(\text{acac})_2]$ -PA, (E): $[\text{Co}(\text{acac})_2]$ -PA, (F): $[\text{Cr}(\text{acac})_3]$ -PA, (G): $[\text{Al}(\text{acac})_3]$ -PA, (H): $[\text{Zr}(\text{acac})_4]$ -PA.

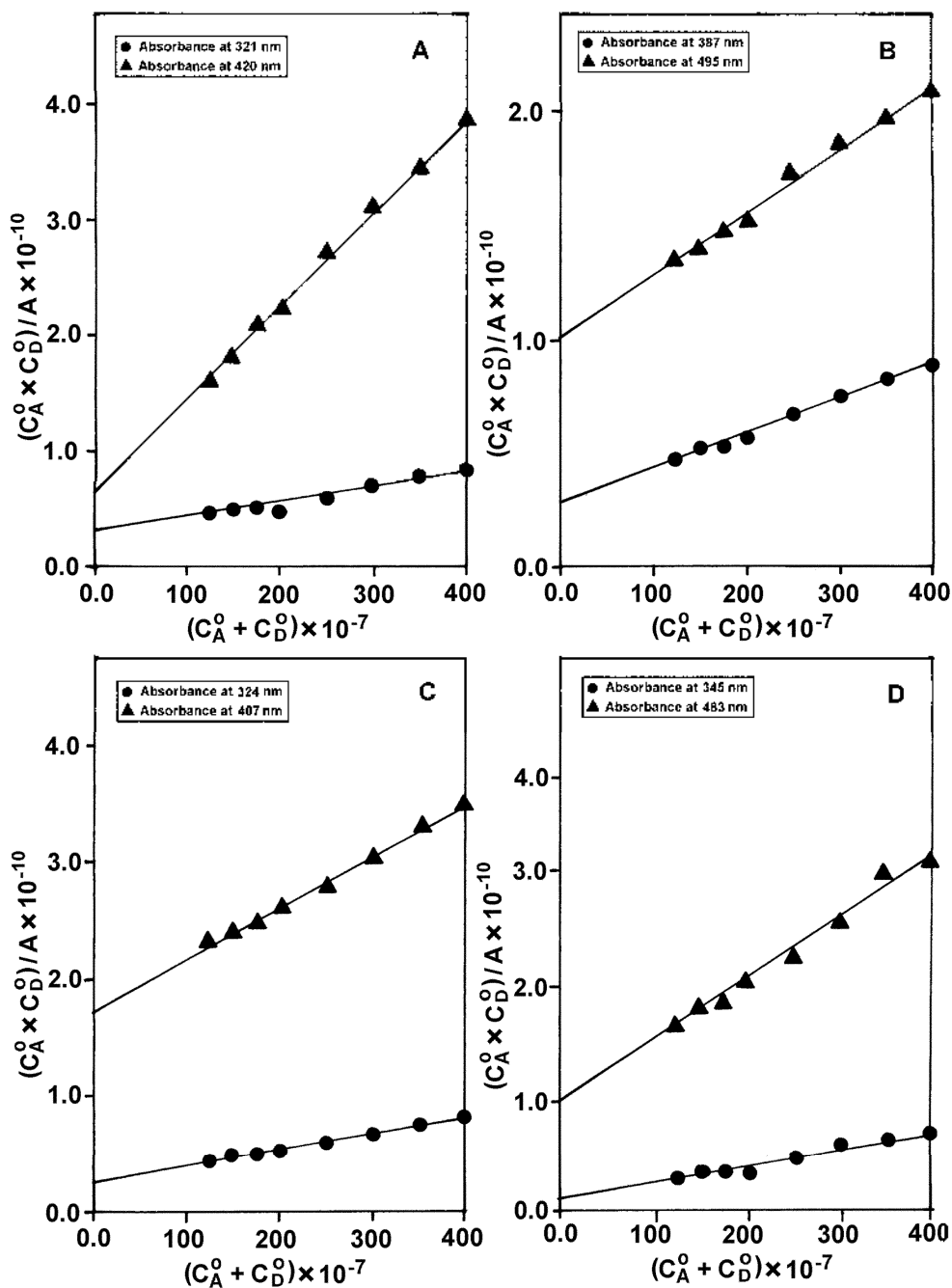


Fig. 3. (Continued)

π -acceptor (PA) and the donor $[M(\text{acac})_n]$ (where $n = 2$ for Cu(II), Ni(II) and Mn(II); $n = 3$ for Fe(III), Co(III), Cr(III) and Al(III); $n = 4$ for Zr(IV)), respectively, while A is the absorption of the strong bands

around 321 and 420 nm for $[\text{Cu}(\text{acac})_2(\text{PA})]$; 387, 411 and 495 nm for $[\text{Ni}(\text{acac})_2(\text{PA})]$; 324, 376 and 407 nm for $[\text{Mn}(\text{acac})_2(\text{PA})]$; 345, 405 and 483 nm for $[\text{Fe}(\text{acac})_3(\text{PA})]$; 319, 369 and 450 nm for $[\text{Co}(\text{acac})_2(\text{PA})]$.

Table 4. Spectrophotometric results of CT-complexes of $[M(\text{acac})_n(\text{PA})]$ (where $n=2$ for $M=\text{Cu}(\text{II}), \text{Ni}(\text{II}), \text{Mn}(\text{II})$; $n=3$ for $M=\text{Fe}(\text{III}), \text{Co}(\text{III}), \text{Cr}(\text{III}), \text{Al}(\text{III})$; $n=4$ for $M=\text{Zr}(\text{IV})$) in CHCl_3 .

Complexes	$K (\text{L} \cdot \text{mol}^{-1}) \times 10^{-4}$	$\lambda_{\text{max}} (\text{nm})$	$\epsilon_{\text{max}} (\text{mol}^{-1} \text{cm}^{-1}) \times 10^{-6}$
$[\text{Cu}(\text{acac})_2(\text{PA})]$	4.27	321	0.781
	12.5	420	0.125
$[\text{Ni}(\text{acac})_2(\text{PA})]$	5.00	387	0.667
	2.67	495	0.370
$[\text{Mn}(\text{acac})_2(\text{PA})]$	4.92	324	0.781
	2.41	407	0.238
$[\text{Fe}(\text{acac})_3(\text{PA})]$	7.00	345	0.893
	4.90	483	0.200
$[\text{Co}(\text{acac})_3(\text{PA})]$	4.00	319	1.000
	7.54	450	0.076
$[\text{Cr}(\text{acac})_3(\text{PA})]$	6.07	361	0.599
	1.62	424	0.185
$[\text{Al}(\text{acac})_3(\text{PA})]$	12.8	358	0.156
	2.67	423	0.178
$[\text{Zr}(\text{acac})_4(\text{PA})]$	6.15	360	0.250
	3.20	440	0.167

361 and 424 nm for $[\text{Cr}(\text{acac})_3(\text{PA})]$; 358 and 423 nm for $[\text{Al}(\text{acac})_3(\text{PA})]$ and 360 and 440 nm for $[\text{Zr}(\text{acac})_4(\text{PA})]$ complexes. The data obtained throughout these calculations are given in Table 3(A-H). Plotting the values of the $C_{\text{D}}^{\text{D}} \cdot C_{\text{D}}^{\text{D}}/A$ against $C_{\text{D}}^{\text{D}} + C_{\text{D}}^{\text{D}}$ values for each donor, a straight line is obtained with a slope of $1/\epsilon$ and intercept of $1/K\epsilon$ as shown in Fig. 3(A-H), for the reactions of various $[M(\text{acac})_n]$ with PA respectively in CHCl_3 . The values of both K and ϵ associated with these complexes $[\text{Cu}(\text{acac})_2(\text{PA})]$, $[\text{Ni}(\text{acac})_2(\text{PA})]$, $[\text{Mn}(\text{acac})_2(\text{PA})]$, $[\text{Fe}(\text{acac})_3(\text{PA})]$, $[\text{Co}(\text{acac})_3(\text{PA})]$, $[\text{Cr}(\text{acac})_3(\text{PA})]$, $[\text{Al}(\text{acac})_3(\text{PA})]$ and $[\text{Zr}(\text{acac})_4(\text{PA})]$ are given in Table 4. These complexes show high values of both the formation constant K and the extinction coefficients ϵ . These high values of K confirm the expected high stabilities of the formed CT-complexes as a result of the expected high donation of the metal acetylacetonates $[M(\text{acac})_n]$.

Fig. 4(A-H) shows the infrared spectra of the formed CT-complexes, $[\text{Cu}(\text{acac})_2(\text{PA})]$, $[\text{Ni}(\text{acac})_2(\text{PA})]$, $[\text{Mn}(\text{acac})_2(\text{PA})]$, $[\text{Fe}(\text{acac})_3(\text{PA})]$, $[\text{Co}(\text{acac})_3(\text{PA})]$, $[\text{Cr}(\text{acac})_3(\text{PA})]$, $[\text{Al}(\text{acac})_3(\text{PA})]$ and $[\text{Zr}(\text{acac})_4(\text{PA})]$.

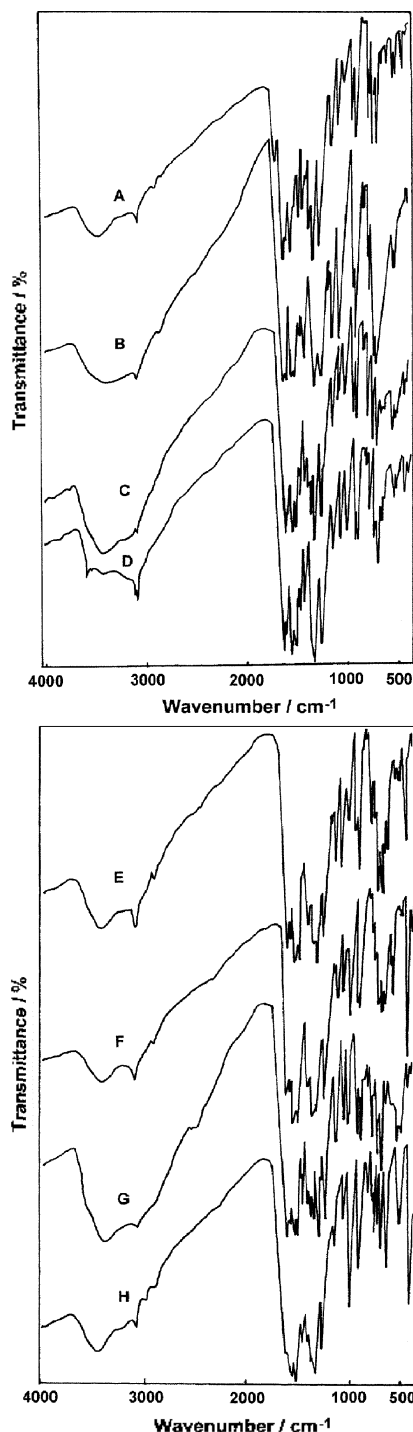


Fig. 4. Infrared spectra of: (A): $[\text{Cu}(\text{acac})_2(\text{PA})]$ (E): $[\text{Co}(\text{acac})_3(\text{PA})]$, (B): $[\text{Ni}(\text{acac})_2(\text{PA})]$ (F): $[\text{Cr}(\text{acac})_3(\text{PA})]$, (C): $[\text{Mn}(\text{acac})_2(\text{PA})]$, (G): $[\text{Al}(\text{acac})_3(\text{PA})]$, (D): $[\text{Fe}(\text{acac})_3(\text{PA})]$, (H): $[\text{Zr}(\text{acac})_4(\text{PA})]$.

Table 5. Infrared frequencies^{a)} and tentative assignments for $[M(\text{acac})_n(\text{PA})]$ (where $n=2$ for $M=\text{Cu(II)}$, Ni(II) , Mn(II) ; $n=3$ for $M=\text{Fe(III)}$, Co(III) , Cr(III) , Al(III) ; $n=4$ for $M=\text{Zr(IV)}$) complexes

Frequencies ^{a)}								Assignments ^{b)}
[M(acac) _n (PA)]								
Cu(II)	Ni(II)	Mn(II)	Fe(III)	Co(III)	Cr(III)	Al(III)	Zr(IV)	
3455 s, br	3398 s, br	3484 sh 3427 br 3341 sh	3556 ms 3398 ms, br	3413 s, br	3427 s, br	33845 s,br	3427s,br	v(O-H)
3213 w,br	3199 w,br	3156 br	3227 sh	3099 s	3084 s	3199 w,br	3241 sh	v(C-H); M(acac) _n
3070 ms	3099 ms	3084 w	3084 s	2999 sh	2984 sh	3070 ms	3070 mw	v(C-H); [-CH-], PA
2913 vw	2925 w, sh	2927 sh	2927 vw	2913 w	2956 vw 2913 w	2956 vw 2913 vw	2984 mw 2899 vw	v(CH ₃); M(acac) _n
1828 ms	1842 s	1870 s	1870 ms	1870 ms	1870 ms	1842 s	1842 mw	v(NO ₂); PA
1685 s	1828 s	1628 s	1628 s	1628 s	1628 s	1628 s	1613 sh	v(C=O); M(acac) _n
1628 s	1613 s	1613 vw	1613 ms			1613 w		
1599 w	1556 s	1556 s	1556 s	1599 s	1599 s	1556 s	1571 s	v(C=C); ring breathing
1556 s	1528 s	1528 s	1528 s	1556 s	1556 s	1528 s	1528 s	bands v(C=O); M(acac) _n
				1528 s	1513 s			v(C=C); M(acac) _n
1485 w	1485 mw	1799 mw	1499 vw	1485 sh	1428 s	1499 w	1456 s	δ (CH);
1471 s	1456 vw	1428 s	1485 ms	1428 s		1471 s	1413 mw	deformation -(CH)-
1428 s	1428 vs		1442 vs			1428 ms		
1385 vv	1371 sh	1399 w	1371 sh	1385 w	1385 s	1399 s	1385 sh	v(C-C); M(acac) _n
1356 ms	1342 s	1371 s	1342 vs	1342 s	1342 s	1371 s	1356 s	v(C-N); PA
1328 vs	1313 sh	1328 vs		1314 vv	1313 sh	1328 vs		
1271 vs	1271 s	1256 vs	1285 vs	1272 vs	1271 vs	1299 vw	1271 vs	v(C-C)-v(C-CH ₃)
1142 s	1185 ms	1156 vs	1156 vs	1171 vv	1185 vv	1271 vs	1156 s	δ (CH); in-plane bend
1057 s	1156 vs	1071 vs	1056 vs	1157 ms	1171 w	1228 sh	1056 s	v(C-O); PA
	1099 vs	999 vs	1014 vs	1128 vs	1157 vs	1142 vs	1014 vs	δ (CH ₃); rock;
				1071 vs	1071 vs	1071 vs		M(acac) _n
				1014 s	1014 vs	1028 vs		
928 s	928 ms	928 vs	942 s	928 s	928 s	999 sh	914 vs	δ (CH); -(CH)-
899 vs	914 vs	899 vs	928 ms	914 vs	914 s	928 vs	842 s	v(C-CH ₃)+v(C-O);
821 w	828 ms	828 ms	914 ms	843 ms	814 w	914 vs	814 ms	M(acac) _n
			843 w			857 vw		δ (ONO); PA
			814 ms			828 s		
799 s	799 s	785 vs	799 w	799 w	799 s	785 s	799 ms	δ (CH); out-of plane bend
778 s	771 vs	742 vs	771 s	772 s	785 ms	742 s	785 s	
743 vs	742 s		743 s	757 vw	771 w	728 vw	742 s	
			728 ms	728 s	728 s		728 ms	
699 vs	714 s	699 s	714 vs	699 vs	699 s	714 vs	714 vs	Ring def. -v(M-O)
			685 s	671 ms	671 s	671 s		
649 ms	657 sh	642 w	614 vw	657 ms	657 ms	614 w	657 vs	δ (C-CH ₃); M(acac) _n
614 ms		628 vw		628 s	614 mw			+v(M-O)
557 s	557 ms	599 vw	557 s	557 ms	585 s	557 ms	528 vs	Ring def. -v(M-O)-
528 s	542 ms	542 ms	528 ms	528 ms	542 mw	528 mw	500 sh	δ (ONO); PA-Skeletal
450 s	471 vw	514 w	457 s	457 vs	514 mw	457 s	428 vs	vib.
414 vw	414 vw	442 ms	414 ms	442 vw	457 vs	428 vw	414 sh	
		428 vw			414 ms	414 w		

^{a)}s=strong; w=weak; m=medium; sh=shoulder; v=very and br=broad

^{b)}v=stretching; and δ =bending.

respectively. The spectral bands of the formed CT-complexes and their band assignments are reported in Table 5. The formation of the $[M(acac)_n]$ -PA, CT-complexes are strongly supported by the observation of the main infrared bands for both reactants $[M(acac)_n]$ and acceptor (PA) in the product spectra. However, the bands of the $[M(acac)_n]$ and acceptor in the spectra of the new CT-complexes show small shifts in the frequency values as well as some changes in their intensities compared with those of the free $[M(acac)_n]$ base and acceptor. This could be attributed to the expected symmetry and electronic structure changes upon the formation of CT-complexes.

Moreover, in general, the IR spectra of the molecular complexes $[M(acac)_n]$ ($M=Cu(II)$, $Ni(II)$, $Mn(II)$, $Fe(III)$, $Co(III)$, $Cr(III)$, $Al(III)$ and $Zr(IV)$) with picric acid indicate that the single $\nu(NO_2)$ band of PA shifted to lower wavenumber values on complexation.

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