(Acetylacetonato)(*N,N,N',N'*-tetramethylethylenediamine)copper(II) Tetraphenylborate as a Solvent Basicity Indicator

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Synopsis. The title complex, [Cu(acac)(tmen)]BPh_4, is a color indicator for solvent basicity which serves better than the corresponding perchlorate in very weak donor solvents owing to its reluctance in ion-pair formation. The complex cation $[Cu(acac)(tmen)]^+$ decomposes in very strong donor solvents, but these indicators may still be used in them with some care.

(Acetylacetonato)(*N,N,N',N'*-tetramethylethylenediamine)copper(II) perchlorate, abbreviated as [Cu(acac)(tmen)]ClO_4, is known to be strongly solvatochromic, owing to the subtle structure changes caused by the solvation processes.[1,2] The coordination center which determines the position of the visible d-d band is extremely sensitive to nucleophilic solvent attack; this fact led to the proposal to use it as a color indicator for solvent basicity, which is expressed in Gutmann's donor number (DN).[2,3]

The use of this complex to estimate the DN of solvents gives reasonably good results when the DN lies between 5 and 30. However, anomalies appear in very weak or very strong donor solvents. As can be seen from the first column of Table 1, the λ_{max} value of this complex decreases with the decrease of DN in going from pyridine to nitromethane, but when the basicity gets smaller it increases notably again. Moreover, in such very weak donor solvents, the λ_{max} values become slightly concentration dependent, decreasing by a few nanometers upon strong dilution. Concentration dependence of λ_{max} appears again, and much more strongly, in very strong donor solvents, but here the λ_{max} increases with dilution.

In order to understand these anomalies better, the tetraphenylborate of the same complex cation was prepared, and its spectral behavior was compared with that of the perchlorate.

Experimental

Preparation of [Cu(acac)(tmen)]BPh_4. 10 g (ca. 0.026 mol) of twice recrystallized [Cu(acac)(tmen)]ClO_4[1] was dissolved in 120 ml of water, and 50 ml of a warm aqueous solution containing 12 g (ca. 0.035 mol) of $NaBPh_4$ was added with stirring. The pale red violet precipitate obtained was filtered off, washed with warm water, and dried in vacuo for several hours at 30 °C. Found: C, 70.34; H, 7.27; N, 4.70%. Calcd for $C_{35}H_{43}BCuN_2O_2$: C, 70.29; H, 7.25; N, 4.68%.

Solvents. The solvents used were all purified according to the literature.

Spectral Measurements. Use was made of a Cary 17 spectrophotometer, with quartz cells of various path lengths. Measurements were made at room temperature (ca. 20 °C).

Results and Discussion

As can be seen from the second column of Table 1, the visible spectra of [Cu(acac)(tmen)]BPh_4 in various solvents of DN>5 are very similar to those of the perchlorate, but the anomalies in very weak donor solvents disappear. The λ_{max} value continues to decrease, even in these solvents, with the decrease of solvent basicity, which can be expressed in terms of Schmid's DN_B,[4] and its concentration dependence is nearly imperceptible. The difference in color between the tetraphenylborate and the perchlorate in such a solvent can be quite large; for example, they are red and blue, respectively, in chlorobenzene, and the difference in their λ_{max} amounts to ca. 100 nm.

Now the curves shown in Fig. 1 reveal that, in addition to the d-d band, there is a continuous background absorption in the blue part of the spectrum, which seems to be the tail of a strong CT band in the near

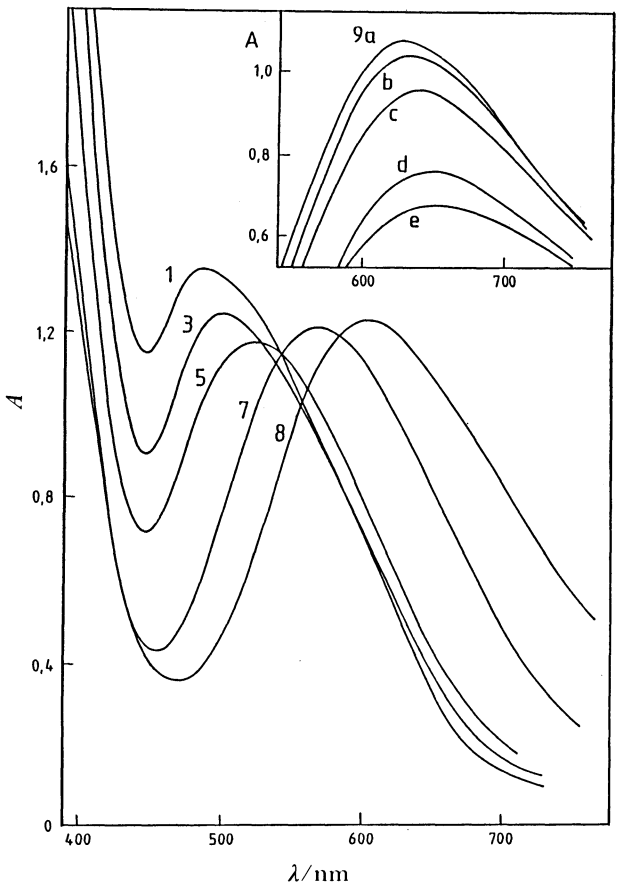

Fig. 1. Visible absorption spectra of [Cu(acac)(tmen)]BPh_4 in various solvents. Notations of the solvents: see Table 1. Concn/M: 0.1, path length/cm: 0.1. Inset: Concentration dependence of the spectrum of [Cu(acac)(tmen)]ClO_4 in pyridine. Concn/M: 0.092(a), 0.046(b), 0.023(c), 0.0092(d), 0.0046(e); path length/cm: 0.1(a), 0.2(b), 0.4(c), 1(d), 2(e). (A= absorbance).

Table 1. λ_{max} of the d-d Band of [Cu(acac)(tmen)]X in Various Solvents

	Solvent	λ_{max}/nm			DN/DN_B[a]
		X=ClO_4	X=BPh_4		
			Observed	Corrected	
1	Dichloromethane (10^{-2} M[b])	550[c]	488	515	(1.2)
2	Chlorobenzene (10^{-3} M)	≈572[c]	480	520	(2.2)
3	1,2-Dichloroethane (10^{-2} M)	≈543[c,d]	498	520	(2.9)
4	Nitrobenzene (10^{-3} M)	533	490	522	(3.7)
5	Nitromethane	532[d]	527	530	(4.8)
6	Acetonitrile	578[d]	573		14.1
7	Acetone	571[d]	569		17.0
8	N,N-Dimethylformamide	603[d]	602		26.6
9	Pyridine (10^{-1} M)	624[e]	623[e]	613[f]	33.1
10	2-Picoline (10^{-2} M)	624[e]	620[e]		—

a) DN_B in parentheses. b) 1 M=1 mol dm^{-3}. c) Slightly concentration dependent. d) From the literature.[1,3] e) Strongly concentration dependent. f) Cf. Table 2.

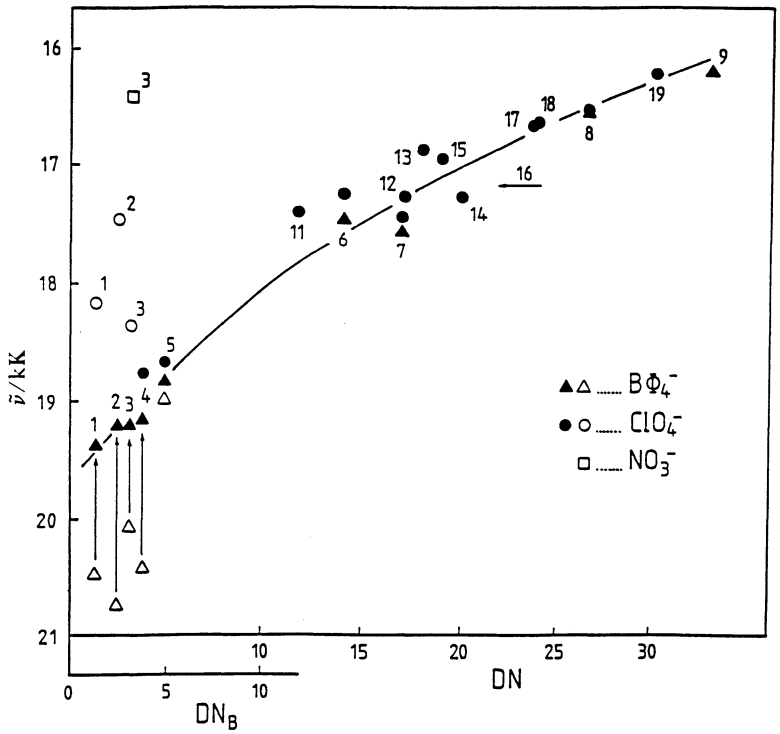

Fig. 2. A plot of the wavenumbers of the d-d band ($\tilde{\nu}_{max}$) against DN or DN_B. Notations of the solvents 1—9: see Table 1. Solvents 11 to 19 correspond, respectively, to benzonitrile, ethyl acetate, water, tetrahydrofuran, methanol, *t*-butyl alcohol, trimethyl phosphate, formamide, and DMSO. For solvents 1—5, DN_B values were used instead of DN. Full triangles 1 to 5 denote corrected values, while open triangles denote observed ones (cf. Table 1). Open circles, and a square for the nitrate, denote the cases where remarkable ion-pair formation takes place. The arrow for 16 indicates a range for its DN estimated from its DN_B.[4] (kK=10^3 cm^{-1}).

ultraviolet. With the decrease of DN or DN_B, this absorption is shifted toward the red, and overlaps remarkably with the d-d band in very weak donor solvents. So the λ_{max} values of the d-d band in such solvents should be corrected for this overlap. This correction was made by assuming that the d-d band in these solvents has the same $\tilde{\nu}$-symmetrical, pseudo-Gaussian shape as in other solvents; the obtained values are given in the third column of Table 1.

When the $\tilde{\nu}$-values corresponding to the λ_{max} values in Table 1 are plotted against DN or DN_B, it can be seen that the points for the tetraphenylborate (full triangles) and those for the perchlorate (full circles) lie along a smooth curve (Fig. 2). However, the points for the latter in three solvents 1—3 deviate strongly from the curve (open circles), confirming that the tetraphenylborate is a better solvent basicity indicator than the perchlorate.[5] The fact that this deviation tends to

Table 2. Variation of λ_{max} of [Cu(acac)(tmen)]BPh_4 in Pyridine with the Addition of tmen

[tmen]/M	0	0.033	0.13	0.27	0.40	∞[a]
λ_{max}/nm	623	619	616	615	614	613

a) Extrapolated by plotting λ_{max} against (1/[tmen]).

increase with the decrease of DN_B supports the view that ion-pair formation, i.e., weak coordination of ClO_4^- on the chelate plane, is responsible for it, which was formerly proposed by Fukuda et al.[6] to explain this type of spectral anomaly found in dichloroethane. In the case of the tetraphenylborate, such an ion-pair formation will not occur effectively since BPh_4^- is so large and inert; the regular spectral trend continues, therefore, in very weak donor solvents with no anomaly.

As to the anomaly in very strong donor solvents, there is no marked difference between the two complex salts. This anomaly is the result of the decomposition of the chelate cation caused by solvent attack. In the case of pyridine, it seems that the tmen ligand is driven off, since the addition of tmen to the solution apparently suppresses the decomposition, shifting λ_{max} to the blue (Table 2). With increasing tmen, the λ_{max} approaches a limit (613 nm); this may be taken as the λ_{max} value for the solvated complex cation [Cu(acac)(tmen)]$^+$ in pyridine, as the corresponding point on Fig. 2 is at a reasonable spot. The present indicators may still be used in such a strong donor solvent, therefore, by adding excess tmen to the solution.[7]

The solutions of the two complex salts in strong donor solvents are thermochromic, becoming more greenish on heating. This fact indicates that the decomposition equilibria in them, e.g.,

$[Cu(acac)(tmen)]^+ + npy \rightleftarrows [Cu(acac)(py)_n]^+ + tmen$

are shifted to the right-hand side by heating.

References

1) Y. Fukuda and K. Sone, *Bull. Chem. Soc. Jpn.*, **45**, 465 (1972).

2) K. Sone and Y. Fukuda, "Ions and Molecules in Solution," ed by N. Tanaka, H. Ohtaki, and R. Tamamushi (Studies in Phys. and Theoret. Chem., Vol. 27), Elsevier, Amsterdam (1983), pp. 251—266.

3) R. W. Soukup and R. Schmid, *J. Chem. Educ.*, **62**, 459 (1985).

4) DN_B is a solvent polarity parameter derived from the linearity between DN and the frequency shift of the O-D vibration of CH_3OD in various solvents (Koppel and Palm's B value), and can be taken as a substitute for DN when the latter is unknown. Cf. R. Schmid, *J. Sol. Chem.*, **12**, 135 (1983); R. Schmid and V. N. Sapunov, "Non-formal Kinetics," Verlag Chemie, Weinheim (1982), Chap. 7.

5) Some authors are dubious about the significance of the concept of DN for protic solvents like water, formamide or alcohols (cf., e.g., L. L. Rusnak, E. S. Yang, and R. B. Jordan, *Inorg. Chem.*, **17**, 1810 (1978); M. Munakata, S. Kitagawa, and M. Miyazima, *ibid.*, **24**, 1638 (1985); M. H. Abraham, *Pure Appl. Chem.*, **57**, 1055 (1985)). In the present case, however, no remarkable deviation of such solvents from the general trend is observable. Of course, the donor ability of a highly structured solvent is always some function of the acceptor strength of the solute. Hence it seems that the acceptor ability of the cation [Cu(acac)(tmen)]$^+$ is essentially similar to that of $SbCl_5$, the reference compound for the DN scale.

6) Y. Fukuda, A. Shimura, M. Mukaida, E. Fujita, and K. Sone, *J. Inorg. Nucl. Chem.*, **36**, 1265 (1974); cf. also Fig. 1 in Ref. 2 and Footnote in Ref. 1.

7) I. Persson (*Pure Appl. Chem.*, **58**, 1153 (1986)) has collected more data on the λ_{max} of [Cu(acac)(tmen)]ClO_4 and [Cu(acac)(tmen)]BPh_4 in strong donor solvents, obtaining information on the latter complex from one of us (R. W. S.). He stated that there is a good correspondence between λ_{max} and DN even when the latter is very high (ca. 50), seemingly without taking the decomposition of the complexes into account.