The Heterotrimetallic Complex [Ni(acacen)KLa(pta)$_4$]: Structural and Thermochemical Studies

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The heterotrimetallic species [Ni(acacen)KLa(pta)$_4$] [H$_2$acacen and Hpta being *N,N′*-ethylenebis(acetylacetonimine) and 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione, respectively] was obtained by interaction of Ni(acacen) with KLa(pta)$_4$ in chloroform. From the X-ray, single crystal structure determination, the potassium cation acts as a bridge between the complex anion [La(pta)$_4$]$^-$ and the neutral complex Ni(acacen). Sublimation, thermal behaviour, pressure, and composition of the vapour phase have been investigated for both [Ni(acacen)KLa(pta)$_4$] and the parent complexes Ni(acacen) and KLa(pta)$_4$, by means of thermal analysis and mass spectrometry using a Knudsen cell. The heterotrimetallic molecule was not found in the saturated vapour. Two processes take place upon heating: [Ni(acacen)KLa(pta)$_4$]$_{(s)}$ → [KLa(pta)$_4$]$_{(s)}$ + Ni(acacen)$_{(g)}$ and [KLa(pta)$_4$]$_{(s)}$ → [KLa(pta)$_4$]$_{(g)}$. The standard free energy of formation for [Ni(acacen)KLa(pta)$_4$] have been estimated ($\Delta G_f{}^0{}_{380K} = -6.1\pm2$ kJ/mol). [Ni(acacen)KLa(pta)$_4$] can be sublimed completely at low pressure because both parent complexes KLa(pta)$_4$ and Ni(acacen) are volatile.

Introduction

Volatile heterometallic complexes are interesting as prospective single-source precursors for the growth of heterometallic thin-film materials by chemical vapour deposition from metal-organic precursor molecules (MOCVD).[1] The coordination chemist′s problem is then to combine at the least two metal elements, into a congruently vaporizing metal-organic complex. Generally, the metal elements do not belong to the same chemical family, and they present different metal complex chemistries and thermochemistries. Various synthetic strategies can be applied.[1] In order to prepare volatile complexes incorporating a *d* and an *f* or an *s* element, we have developed a strategy based on the use of *d* metal complexes as neutral ligands to coordinatively saturate an *f* or an *s* element cation in one of its β-diketonates.[2−5]

We present here results about an unusual heterotrimetallic complex, which results from interaction between the heterobimetallic complex KLa(pta)$_4$ and Ni(acacen).

Results and Discussion

Synthesis and Crystal Structure of [Ni(acacen)KLa(pta)$_4$]

The heterotrimetallic complex [Ni(acacen)KLa(pta)$_4$] was obtained as a single-phased, red-brown, crystalline product by simple interaction of Ni(acacen) with KLa(pta)$_4$ in chloroform. It crystallises in the triclinic system, with a space group of $P\bar{1}$, and unit-cell volume 2769 Å^3. The unit-cell comprises two centrosymmetrically related asymmetric units.

The asymmetric unit is made of one of each constituent: a complex anion [La(pta)$_4$]$^-$, a cation K$^+$, and a neutral complex Ni(acacen) (Figure 1). The potassium acts as a link

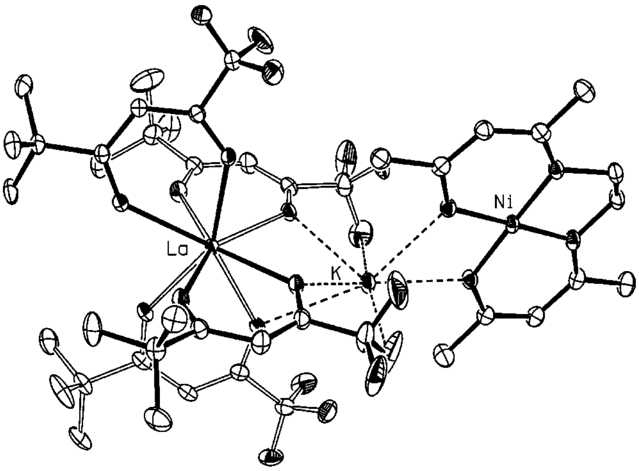

Figure 1. The heterotrimetallic entity [Ni(acacen)KLa(pta)$_4$]; ellipsoids are at their 30% probability level; ellipsoids with octant shading are for non-carbon atoms

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Table 1. Selected distances [Å] and angles [deg] in $[Ni(acacen)KLa(pta)_4]$

Around K		Around La		Around Ni	
K−O(2)	2.661(3)	La−O(1b)	2.421(2)	Ni−O(1)	1.857(2)
K−O(1a)	2.677(3)	La−O(2d)	2.439(2)	Ni−O(2)	1.859(3)
K−O(1c)	2.731(3)	La−O(2a)	2.470(3)	Ni−N(1)	1.853(3)
K−O(1)	2.742(3)	La−O(2b)	2.490(3)	Ni−N(2)	1.858(3)
K−F(1c)	2.843(5)	La−O(2c)	2.494(3)	O(1)−Ni−O(2)	84.01(11)
K−O(1d)	2.914(3)	La−O(1a)	2.521(3)	O(1)−Ni−N(1)	94.73(13)
K−F(1a)	2.949(4)	La−O(1c)	2.532(3)	O(2)−Ni−N(2)	94.16(13)
		La−O(1d)	2.532(2)	N(1)−Ni−N(2)	87.21(14)
K···La	3.9421(11)				
K···Ni	3.7780(11)			Ni···Ni[a]	4.8000(14)
				Ni···Ni[b]	6.5691(15)
				N(1)−C(11)−C(12)−N(2)	-35.9(4)

[a] Code of symmetry operations: $1 - x, - y, 1 - z$. − [b] $-x, -y, 1 - z$.

between the two metal complexes, being in contact with the two oxygen atoms of Ni(acacen), and three oxygen and two fluorine atoms of $[La(pta)_4]^-$. Selected bond lengths and angles are presented in Table 1.

Around La (Figure 2), the four triangles LaO(1a)O(2a), LaO(1b)O(2b), LaO(1c)O(2c), and LaO(1d)O(2d) are almost perpendicular to each other, making angles ranging from 85.5(1)° to 89.6(1)° with each other. Dihedral angles about O(1i)O(2i) between these planes and respective mean planes of atoms O(1i), O(2i), C(1i), C(2i), C(3i), C(4i), C(5i) are 12.4(1)° and 12.9(1)° for ligands *b* and *d*, and 4.0(2)° and 4.2(2)° for ligands *a* and *c*, respectively. The coordination polyhedron around La is close to a bicapped trigonal prism, with O(1a)O(2a)O(1b) and O(1d)O(2d)O(2c) as the triangular faces, O(2b) and O(1c) at the capping vertices.

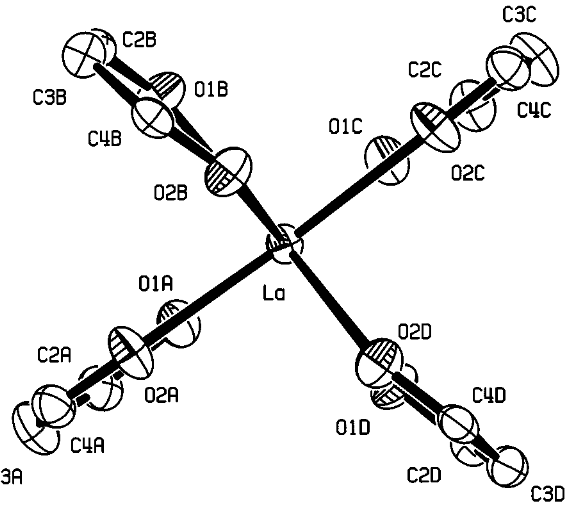

Figure 2. A view of the $La(pta)_4^-$ entity; for the sake of clarity, *tert*-butyl and trifluoromethyl groups have been omitted

Cerium(IV) in $Ce(pta)_4$ and cerium(III) in $(NH_4)Ce(pta)_4$ have been recently reported to have a square antiprism coordination geometry.[6] Distortion from expected square antiprism in the present compound is likely to result from the cation K^+, which tightly binds two *pta* oxygen atoms: K−O(1a) = 2.677(3) Å and K−O(1c) = 2.731(3) Å. Potassium next neighbouring atoms are the *acacen* oxygen atoms O(1) and O(2) at 2.742(3) Å and 2.661(3) Å, respectively, the *pta* oxygen O(1d) at 2.914(3) Å, and the fluorine atoms F(1c), F(1a), F(2d), and F(2a) at 2.843(4) Å, 2.949(4) Å, 3.295(3) Å, and 3.358(4) Å, respectively.

In Ni(acacen) (Figure 3−5), slight deviations from planarity are evident, besides the torsion angle N(1)C(11)C(12)N(2) of −35.9(4)°. The N_2O_2 environment of the nickel atom is slightly tetrahedrally distorted, with atom to mean plane distances of ±0.04 Å. The planes defined by atoms Ni, O(1), and N(1) on one hand and Ni, O(2), and N(2) on the other hand make an angle of 3.5(3)°. In both ketoimine moieties, planar OC_3 and NC_3 parts make an angle of circa 5° with each other. The Ni(acacen) entities are related by inversion. They partially overlap, giving rise to stacks parallel to the *a* axis with distances between mean planes alternatively equal to 3.66 Å for inversion through (1/2, 0, 1/2), and to 3.85 Å for inversion through (0, 0, 1/2). Figure 3 and Figure 4 show that the overlap is more extended for entities separated by 3.66 Å than by 3.85 Å. Intra-stack Ni···Ni distances are 4.800(1) Å and 6.569(1) Å, alternatively (Figure 5).

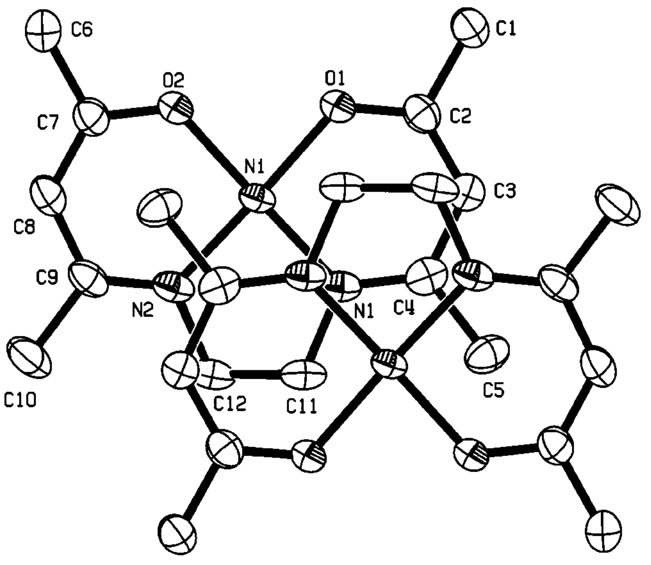

Figure 3. Overlap scheme of centrosymmetrically related Ni(acacen) entities in $[Ni(acacen)KLa(pta)_4]$ through inversion at (1/2, 0, 1/2)

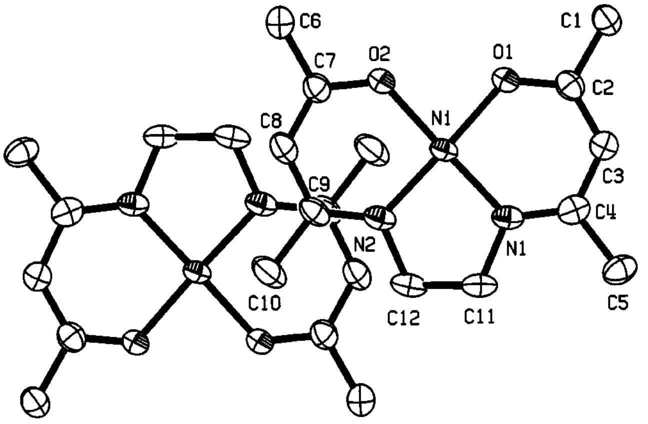

Figure 4. Overlap scheme of centrosymmetrically related Ni(acacen) entities in [Ni(acacen)KLa(pta)$_4$] through inversion at (0, 0, 1/2)

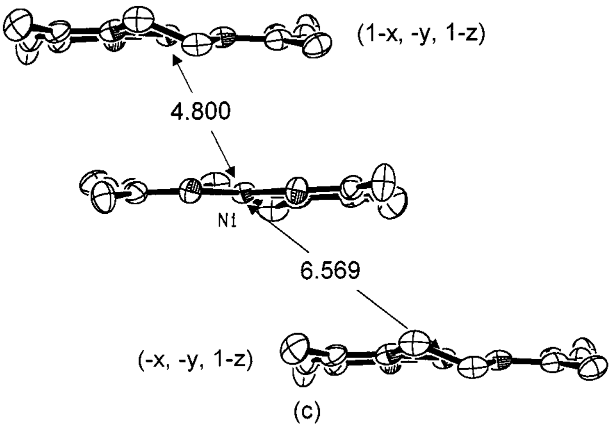

Figure 5. Overlap schemes of centrosymmetrically related Ni(acacen) entities in [Ni(acacen)KLa(pta)$_4$], a side view of the stacking repeat unit

Table 2. Tentative inventory of van der Waals contacts in [Ni(acacen)KLa(pta)$_4$]

F···CH_3		CH_3···CH_3	
F(2a)···C(52d)[a]	3.243(6)	C(51a)···C(52b)[b]	4.007(7)
F(2a)···C(10)[c]	3.324(5)	C(52a)···C(51b)[d]	3.950(7)
F(2b)···C(51d)[a]	3.380(5)	C(53a)···C(53a)[e]	3.427(12)
		C(53b)···C(53d)[b]	3.922(7)
F···CH_2		C(52d)···C(1)[f]	3.876(7)
F(2c)···C(11)[g]	3.222(5)		
F(2c)···C(12)[g]	3.215(5)	CH_3···CH	
F(1d)···C(11)[f]	3.255(5)	C(3b)···C(52a)[h]	3.535(7)
		C(3d)···C(51c)[d]	3.757(6)
F···CH		C(52d)···C(3)[f]	3.976(7)
F(1d)···C(8)[i]	3.419(5)		

[a] Code of symmetry operations: $x, y - 1, z$. – [b] $-x, 1 - y, -z$; – [c] $-x, -y, 1 - z$. – [d] $x - 1, y, z$; – [e] $-x, -y, -z$; – [f] $x, 1 + y, z$; – [g] $1 - x, -y, 1 - z$. – [h] $1 + x, y, z$. – [i] $-x, 1 - y, 1 - z$.

Table 2 shows the results of a screening of van der Waals contacts. They consist of contacts between F atoms and $-CH_3$, $-CH_2$, or $-CH$ groups, and between $-CH_3$ and $-CH_3$ or $-CH$ groups. There are no van der Waals contacts between F atoms.

For Ni(acacen) entities separated by 3.66 Å, the distances from one entity to the centrosymmetrically related one [N(1)···N(1) = 3.66 Å and N(2)···C(4) = 3.70 Å] suggest interactions between π-electrons of partial double bonds N(1)–C(4) and N(2)–C(9). In the same way, a strong interaction between the methyl group about C(5) and electrons delocalized on bonds between atoms O(2), C(7), C(8), C(9), and N(2) of the centrosymmetrically related *acacen* ligand is suggested by the fact that C(5) is at 3.7–3.8 Å from these atoms and at 3.441(4) Å from the mean plane of the ligand. The methylene group about C(11) is possibly involved in the same kind of interaction to a lesser extent: C(11) is at 3.6–3.7 Å from atoms O(1) and N(1) of the related entity and 3.412(5) Å from mean plane of the corresponding *acacen*. For entities separated by 3.85 Å, the methyl group about C(10) for each entity is at 3.630(6) Å from the mean plane of atoms O(2), C(7), C(8), C(9), and N(2) of the related entity.

Thermal Analyses and Vacuum Sublimation

The results of thermal analyses for [Ni(acacen)KLa(pta)$_4$] have been correlated with those for parent complexes KLa(pta)$_4$ and Ni(acacen).

The thermogravimetric analysis curves for KLa(pta)$_4$ and Ni(acacen) are shown in Figure 6, a and 6, b respectively. A single-stepped, quasi total (>98%) weight loss occurs at 165–230 °C and 205–285 °C, respectively for KLa(pta)$_4$ and Ni(acacen). This corresponds predominantly to sublimation. The thermogravimetric curve for [Ni(acacen)KLa(pta)$_4$] (Figure 6, c) shows two stages of weight loss. The major weight loss (70%) occurs in the temperature range 180–330 °C, which corresponds to sublimation. The second, smoother stage (weight loss of about 20%) occurs in the range 330–500 °C. This may correspond to partial thermal decomposition of the complex. The nonvolatile residue amounted to 6% of the initial weight, confirming that sublimation is mainly responsible for the weight loss.

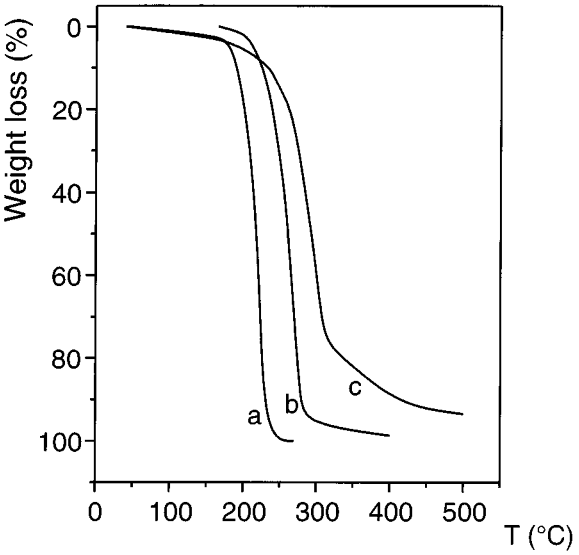

Figure 6. Thermal gravimetric analyses under vacuum (0.01 Torr) for a) KLa(pta)$_4$, b) Ni(acacen), c) [Ni(acacen)KLa(pta)$_4$]

[Ni(acacen)KLa(pta)$_4$] was submitted to isothermal vacuum sublimation (0.01 Torr). The sample was totally sublimed at 200 °C, yielding a single, homogeneous sublimate at the cold end of the reactor tube. Results of elemental analyses for the sublimate were the same as for the starting $[Ni(acacen)KLa(pta)_4]$. However, this experiment did not show whether sublimation occurred with or without dissociation. In order to determine whether $[KLa(pta)_4Ni(acacen)]$ exists in the vapour phase, or dissociates into gaseous $KLa(pta)_4$ and Ni(acacen), which would recombine at the cold part of the reactor, mass-spectrometry experiments were carried out for $[Ni(acacen)KLa(pta)_4]$ and the component complexes $KLa(pta)_4$ and Ni(acacen).

Mass Spectrometry of [Ni(acacen)], $[KLa(pta)_4]$ and $[Ni(acacen)KLa(pta)_4]$

$[KLa(pta)_4]$

The mass spectra of $[KLa(pta)_4]$ were recorded in the temperature range 394−420 K (Table 3). The major species were lanthanum-containing $[La(pta)_3]^+$, $[La(pta)(OCCF_3CH_2]^+$ and $[La(pta)_4]^+$. However, the heterobimetallic molecular ion $[KLa(pta)_4]^+$ was observed over the temperature range, thus indicating that no decomposition of $[KLa(pta)_4]$ into K(pta) and $La(pta)_3$ occurs upon sublimation. At 418 K, the vapour pressure of $[KLa(pta)_4]$ is equal to $4.2 \cdot 10^{-2}$ Pa. Congruent sublimation has been reported for other ionic bimetallic complexes of lanthanide fluorinated β-diketonates. The compound $[NaCe(pta)_4]$ sublimes without decomposition according to published mass spectrometry data.[6] A similar spectrum was obtained for $Cs[Y(hafa)_4]$, which was the first volatile heterobimetallic complex investigated by mass spectrometry.[7] The tendency to form lanthanum-fluorine containing species is supported by our data too (Table 3). The formation of such species upon fragmentation is likely to result from migration of fluorine atoms from the ligands to the metal centre, a process favoured by the hard-acid character of lanthanides.[8]

[Ni(acacen)]

[Ni(acacen)] sublimes congruently in the temperature range 349−412 K. At 393 K, the vapour pressure of [Ni(acacen)] is equal to $1.4 \cdot 10^{-1}$ Pa. The standard enthalpy of sublimation for [Ni(acacen)] was found to be 127.7 ± 0.3 kJ/mol from mass spectrometry data (Table 4), in good agreement with the value of 129.1±0.9 kJ/mol, measured by effusion in the range 402−450 K.[9] [Ni(acacen)] is more volatile than the related nickel Schiff-base complex, Ni(salen), which sublimes in the range 459−545 K.[2] The difference in volatility is likely to result from stronger π interactions between the phenyl groups in solid Ni(salen)[10] with respect to Ni(acacen), which does not contain such groups. [Ni(acacen)] has a volatility that compares with those of nickel acetylacetonate[11] and nickel acetylacetoniminate.[12]

$[Ni(acacen)KLa(pta)_4]$

Mass spectra were recorded at 390 K and 419 K. They show ions containing either Ni, or La, or La and K (Table 3), thus indicating that the heterotrimetallic molecule is not present in the saturated vapour. Relative intensities of La-containing species tend to increase on increasing temperature. It may be inferred that two processes take place upon heating are, accroding to Equation (1) and Equation (2):

$$[Ni(acacen)KLa(pta)_4]_{(s)} \rightarrow [KLa(pta)_4]_{(s)} + Ni(acacen)_{(g)} \qquad (1)$$

$$[KLa(pta)_4]_{(s)} \rightarrow [KLa(pta)_4]_{(g)} \qquad (2)$$

The temperature dependence of ion current intensities was measured for Ni-containing species in the temperature range 350−419 K. The vapour pressure of Ni(acacen) over

Table 3. Intensities of main ion currents (relative units) in mass spectra of $[KLa(pta)_4]$, Ni(acacen) and $[Ni(acacen)KLa(pta)_4)$ (U = 60 eV)

$[KLa(pta)_4]$ (415 K)		[Ni(acacen)] (407 K)		$[Ni(acacen)KLa(pta)_4)]$ (390 K)		$[Ni(acacen)KLa(pta)_4)]$ (419 K)	
$[KLa(pta)_4]^+$	0.12	$[Ni(acacen)]^+$	1.00	$[Ni(acacen)]^+$	1.00	$[Ni(acacen)]^+$	1.00
$[La(pta)_4]^+$	0.64	$[NiOC(CH_3)CH_2C(CH_3)NC]^+$	0.69	$[NiOC(CH_3)CH_2C(CH_3)NC]^+$	0.66	$[NiOC(CH_3)CH_2C(CH_3)NC]^+$	0.26
$[La(pta)_3]^+$	1.00	$[NiOC(CH_3)CH_2NC]^+$	0.10	$[KLa(pta)_4]^+$	0.02	$[KLa(pta)_4]^+$	0.05
$[LaF(pta)_2(OCCF_3)]^+$	0.10	$[CH_3C(O)CH_2CN]^+$	0.08	$[KLa(pta)_3]^+$	0.01	$[KLa(pta)_3]^+$	0.01
$[La(pta)_2]^+$	0.01			$[La(pta)_4]^+$	0.01	$[La(pta)_4]^+$	0.02
$[La(pta)(OCCF_3CH_2]^+$	0.93			$[La(pta)_3]^+$	0.02	$[La(pta)_3]^+$	0.48
$[LaOF(pta)]^+$	0.32			$[La(pta)_2OC(CH_3)_3CHCO]^+$	0.04	$[La(pta)_2OC(CH_3)_3CHCO]^+$	0.05
				$[La(pta)_2OCF_3CHCO]^+$	0.02	$[La(pta)_2OCF_3CHCO]^+$	0.64
				$[La(pta)_2]^+$	0.04	$[La(pta)_2]^+$	0.01
				$[La(pta)OCCF_3CH_2]^+$	0.05	$[LaOCC(CH_3)_3]^+$	0.01
				$[LaOCC(CH_3)]^+{}_3$	0.04		

Table 4. Temperature dependence of saturated vapour pressures of Ni(acacen) and $[Ni(acacen)KLa(pta)_4)]$

Complex	A[a]	B[a]	*T* range [K]	$\Delta_s H^0_T$ [kJ/mol]
Ni(acacen)	6667 ± 155	16.11 ± 0.08	349−412	128 ± 3
$[Ni(acacen)KLa(pta)_4)]$	7633 ± 160	17.74 ± 0.11	350−419	146 ± 10

[a] A and B are coefficients of the equation $\log P_{Pa} = -A/T + B$.

[Ni(acacen)KLa(pta)$_4$] (Table 4) is lower (2.1 10^{-2} Pa at 393 K) than over solid Ni(acacen), due to formation of the heterotrimetallic complex. From measured saturated vapour pressures of Ni(acacen) over [Ni(acacen)KLa(pta)$_4$] and over Ni(acacen), the activity of Ni(acacen) at 380 K was found to be $a_{[\mathrm{Ni(acacen)}]} = 0.15$. The standard free energy of formation of [Ni(acacen)KLa(pta)$_4$] according to Equation (3) was found to be $\Delta G_f^0{}_{380\mathrm{K}} = -6.1 \pm 2$ kJ/mol.

$$[\mathrm{KLa(pta)_4}]_{(s)} + \mathrm{Ni(acacen)}_{(s)} \rightarrow [\mathrm{Ni(acacen)KLa(pta)_4}]_{(s)} \qquad (3)$$

Conclusion

The complex [Ni(acacen)KLa(pta)$_4$] is an interesting example of a heterometallic compound in which a cation, namely K^+, acts as a bridge between two metal complexes. In coordination chemistry, examples of heterometallic compounds with bridging ligands abound, and usually, polydentate ligands act as bridges between two metal centres. One further possibility is to have a neutral metal complex acting as a ligand towards the coordinatively unsaturated metal centre of a second complex, as is the case for instance for the series of complexes of formulae [M(SB)Ln(β-dik)$_3$] (M = Cu, Ni, SB = Schiff base such as *saloph*, *salen*, *acacen*, β-dik = *thd*, *pta*, *hfa*, *fod*) that we are investigating.[2,3] In the case of [Ni(acacen)KLa(pta)$_4$], both complex entities [Ni(acacen)] and [La(pta)$_4{}^-$] are coordinatively saturated, but oxygen donor atoms from ligands *pta* and *acacen* may form additional bridging bonds. It is worth pointing out that some of the fluorine atoms of the β-diketone participate to this bridge, so that the question arises of the existence of such complexes with nonfluorinated β-diketones about the lanthanide cation.

According to thermodynamic data, the energy of interaction between Ni(acacen) and KLa(pta)$_4$] is rather weak. Upon heating, the complex [Ni(acacen)KLa(pta)$_4$] dissociates into its parent complexes Ni(acacen) and KLa(pta)$_4$, and sublimation may be complete thanks to the volatility of both components.

Experimental Section

Preparation and Characterization of the Complex [Ni(acacen)KLa(pta)$_4$]: The starting materials H$_2$(acacen), Ni(acacen), were obtained according to literature methods.[13] The preparation of KLa(pta)$_4$, was adapted from that of NaCe(thd)$_4$.[6] − Elemental analyses (C, H, N) were carried out by the Microanalytical Service of the Moscow State University. − IR spectra were recorded on a Perkin−Elmer 1750 FTIR spectrophotometer for KBr disks in the 4000−300 cm^{-1} region.

[Ni(acacen)KLa(pta)$_4$] was obtained as follows: A solution of Ni(acacen) (112 mg, 0.4 mmol) in 50 mL of chloroform was slowly added to a solution of [KLa(pta)$_4$] (383 mg 0.4 mmol) in chloroform. The red solution was then heated under reflux for 2 h. Slow evaporation of the resulting solution afforded dark red crystals (445 mg, yield 90%). − $C_{44}H_{58}F_{12}KLaN_2NiO_{10}$ (1239): calcd. C 42.61, H 4.68, N 2.26; found C 42.52, H 4.80, N 2.29. − IR: $\tilde{\nu}$ = 2980, 1635, 1540, 1520, 1480, 1425, 1380, 1360, 1285, 1240, 1160, 1120, 975, 950, 915, 840, 800, 760, 700, 650, 545, 485 cm^{-1}.

X-ray Structure Study: Crystal data: formula $C_{44}H_{58}F_{12}KLaN_2NiO_{10}$, mol. weight = 1239.6 amu, monoclinic, $P\bar{1}$, a = 9.984(2), b = 12.455(2), c = 23.064(4) Å, α = 101.68(2)°, β = 98.96(2)°, γ = 91.58(2)°, Z = 2, d = 1.487 g.cm^{-3}, μ = 1.27 mm^{-1}. − Data collection: Stoe Imaging Plate Diffraction System (IPDS), Oxford Cryosystems cooler device, monochromated Mo-K_α radiation, T = 140 K, crystal size 0.75×0.17×0.10 mm, crystal-to-detector distance 80 mm, 208 exposures (2 minutes/exposure), $0 < \varphi < 249.6°$, φ oscillation 1.2°, $1.45 < \theta_{max} < 24.20°$, coverage of the unique set 93%. Measured reflections 21835, observed (expected) unique reflections 8234 (8852). Crystal decay monitored by measuring 200 reflections per image, only statistical fluctuations observed. Intensities corrected for Lorentz and polarisation effects, not for absorption (average cylindrical μr = 0.1). − Structural analysis and refinement: analysis by Patterson and Fourier map techniques, refinement by full-matrix, least-squares techniques, using the SHELX-93 program.[14] All H atoms introduced at calculated positions using a riding model. Anisotropic displacement parameters for non-H atoms: 640 parameters for 8234 reflections. R = 0.034 [7208 $F_o > 4\sigma(F_o)$] and 0.040 for all data, R_w = 0.087, GooF = 1.06 e.

Thermal Analyses: Thermogravimetric and differential thermal analyses under vacuum (0.01 Torr) were carried out on a Sinku-Riko TGD-7000 thermal analyzer, at a heating rate of 10°/min. Isothermal dynamic sublimation experiments were run with samples (100 mg) placed in glass test tubes for periods of 30 min at 200 °C and a pressure of 0.01 Torr. Weight loss was equal to 100%. The sublimate was collected in cold part of reactor and analysed. − $C_{44}H_{58}F_{12}KLaN_2NiO_{10}$ (1239.6) : calcd. C 42.61, H 4.68, N 2.26; found C 42.76, H 4.76, N 1.81.

Mass Spectrometry and Study of the Vapour Phase: The mass spectra of Ni(acacen), KLa(pta)$_4$ and [Ni(acacen)KLa(pta)$_4$] were recorded on a MS 1301 spectrometer having a 50−1500 amu mass range, and using 60 eV ionising electrons. The complexes were vapourised from a Knudsen effusion cell. The ratio of surface of evaporation to surface of the effusion hole was about 600. The cell temperature was measured with a Pt/Pt(Rh) thermocouple (±0.1 K). The experiments were carried out in ranges 349−412 K for Ni(acacen), 394−420 K for KLa(pta)$_4$ and 350−420 K for [Ni(acacen)KLa(pta)$_4$]. The main ion peaks in mass spectra of Ni(acacen), KLa(pta)$_4$ and [Ni(acacen)KLa(pta)$_4$] are given in Table 3.

Vapour pressures *versus* temperature were determined by means of isothermal vapourisation experiments and use of the Herz−Knudsen equation. Enthalpies of sublimation were calculated from the temperature dependencies of ion current intensities by using Clausius−Clapeyron equation and a least-squares method.

Crystallographic data (excluding the structure factor tables) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-147101. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44(1223)336−033; E-mail: deposit@ccdc.cam.ac.uk].

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